Copper-Catalyzed Alkylation of Aliphatic Amines Induced by Visible Light

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Supporting Information

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I. General Information

All manipulations of air-sensitive materials were carried out in oven-dried glassware under an N_2 atmosphere using standard Schlenk or glovebox techniques. 3-Phenylpropylamine (Alfa Aesar), cyclohexanemethylamine (Acros), cyclohexylamine (Sigma-Aldrich), 2-phenoxyethylamine (Alfa Aesar), 3-methoxypropylamine (Sigma-Aldrich), tetrahydrofurfurylamine (Sigma-Aldrich), 2,2-dimethoxyethylamine (Sigma-Aldrich), and 4-chlorophenethylamine (Acros), 4-bromophenethylamine (Oakwood), furfurylamine (Sigma-Aldrich), and thiophene-2-ethylamine (Oakwood) were distilled prior to use. Et_2O, CH_2Cl_2, and CH_3CN were purified and dried using a solvent-purification system that contained activated alumina under argon. CuI (99.999% trace metal basis, Sigma-Aldrich), *rac*-BINOL (Oakwood), BTPP (*tert*-butylimino-tri(pyrrolidino)phosphorane, Sigma-Aldrich), DMF (anhydrous, 99.8%, Sigma-Aldrich), iodocyclohexane (Oakwood), 4-iodotetrahydro-2*H*-pyran (Combi-Blocks), 1-iodo-2-2-dimethylpropane (Sigma-Aldrich), 1,3,5-trimethoxybenzene (≥99%, Sigma-Aldrich), and tetradecane (≥99%, Sigma-Aldrich) were used as received.

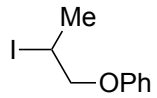
^{1}H, ^{13}C, and ^{31}P NMR data were collected on a Bruker 400 MHz or a Varian 500 MHz spectrometer at ambient temperature unless otherwise noted. FT-IR measurements were

carried out on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory. HRMS and LRMS were acquired using an Agilent 6850 GC, a JEOL JMS-600H MS in fast atom bombardment (FAB) ionization mode, or an Agilent 6200 Series TOF MS with an Agilent G1978A Multimode source in electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) mode. GC analyses were obtained on an Agilent 6890N GC. Flash column chromatography was performed using silica gel (SiliaFlash® P60, particle size 40-63 μm, Silicycle) or using basic alumina (Brockmann I, particle size 50-200 μm, Acros). Blue LED lamps (34 W; Kessil H150-Blue) were used to irradiate the reaction mixtures.

II. Preparation of Electrophiles

The yields have not been optimized.

General Procedure A.[1,2] PPh_3 (1.50 equiv) and imidazole (1.50 equiv) were dissolved in CH_2Cl_2 (~0.3 M), and the resulting solution was cooled to 0 °C. At this temperature, iodine (1.50 equiv) was added slowly in portions, and the resulting mixture was stirred for 10 min. Next, the alcohol (1.00 equiv) was added, and the resulting mixture was allowed to warm to room temperature and stirred overnight. Then, the reaction mixture was poured into hexanes (~3 times the volume of the reaction mixture) and filtered. The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography on silica gel to afford the pure product.



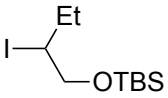
(2-Iodopropoxy)benzene. The title compound was synthesized according to General Procedure A from 1-phenoxypropan-2-ol (1.50 g, 9.86 mmol), PPh_3 (3.88 g, 14.8 mmol), imidazole (1.00 g, 14.8 mmol), and iodine (3.75 g, 14.8 mmol). The product was purified by flash chromatography with silica gel (95:5 → 80:20 hexanes/Et_2O). Colorless liquid; 1.64 g (63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 2H), 6.99 (td, *J* = 7.3, 1.1 Hz, 1H), 6.91 (dd, *J* = 7.7, 1.1 Hz, 2H), 4.46 – 4.30 (m, 1H), 4.25 (dd, *J* = 10.0, 5.5 Hz, 1H), 4.05 (dd, *J* = 10.0, 7.8 Hz, 1H), 2.01 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 129.7, 121.5, 114.9, 74.9, 24.9, 22.4.

FT-IR (neat) 3039, 2970, 2921, 2867, 1598, 1587, 1495, 1455, 1381, 1300, 1240, 1172, 1138, 1104, 1076, 1050, 1030, 1014, 994, 882, 815, 753, 691, 630 cm^{-1}.

HRMS (FAB) *m*/*z* $(M)^+$ calcd for $C_9H_{11}IO$: 261.9855, found: 261.9842.



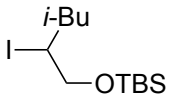
***tert*-Butyl(2-iodobutoxy)dimethylsilane.** The title compound was synthesized according to General Procedure A from 1-((*tert*-butyldimethylsilyl)oxy)butan-2-ol[3] (3.00 g, 14.2 mmol), PPh_3 (5.60 g, 21.4 mmol), imidazole (1.45 g, 21.4 mmol), and iodine (5.42 g, 21.4 mmol). The product was purified by flash chromatography with silica gel (95:5 → 80:20 hexanes/Et_2O). Colorless liquid; 2.66 g (60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 – 3.99 (m, 1H), 3.88 (dd, *J* = 10.6, 5.3 Hz, 1H), 3.74 (dd, *J* = 10.6, 7.9 Hz, 1H), 2.01 – 1.84 (m, 1H), 1.81 – 1.63 (m, 1H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 68.7, 40.5, 29.2, 26.0, 18.5, 14.0, –5.1, –5.2.

FT-IR (neat) 2956, 2929, 2884, 2857, 1471, 1462, 1254, 1137, 1103, 1078, 838, 814, 777 cm^{-1}.

HRMS (FAB) *m*/*z* $(M+H-H_2)^+$ calcd for $C_{10}H_{22}IOSi$: 313.0485, found: 313.0484.



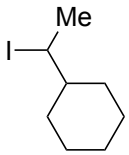
***tert*-Butyl((2-iodo-4-methylpentyl)oxy)dimethylsilane.** The title compound was synthesized according to General Procedure A from 1-((*tert*-butyldimethylsilyl)oxy)-4-methylpentan-2-ol (2.00 g, 8.3 mmol), PPh_3 (3.3 g, 12.5 mmol), imidazole (0.85 g, 12.5 mmol), and iodine (3.2 g, 12.5 mmol). The product was purified by flash chromatography with silica gel (hexanes). Colorless liquid; 1.82 g (64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 – 4.04 (m, 1H), 3.88 (dd, *J* = 10.7, 5.4 Hz, 1H), 3.73 (dd, *J* = 10.6, 7.2 Hz, 1H), 1.92 – 1.77 (m, 1H), 1.78 – 1.64 (m, 1H), 1.61 – 1.51 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.91 (s, 9H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 69.6, 45.3, 37.1, 28.3, 26.0, 23.3, 21.0, 18.5, –5.0, –5.1.

FT-IR (neat) 2955, 2928, 2857, 1470, 1386, 1253, 1140, 1121, 1085, 1035, 1005, 834, 811, 775, 668 cm^{-1}.

HRMS (FAB) *m*/*z* $(M+H)^+$ calcd for $C_{12}H_{28}IOSi$: 343.0949, found: 343.0952.



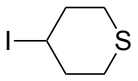
(1-Iodoethyl)cyclohexane. The title compound was synthesized according to General Procedure A from 1-cyclohexylethan-1-ol[4] (3.38 g, 25.6 mmol), PPh_3 (10.1 g, 38.4 mmol), imidazole (2.61 g, 38.4 mmol), and iodine (9.7 g, 38.4 mmol). The product was purified by flash chromatography with silica gel (hexanes). Colorless liquid; 2.13 g (35% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (qd, *J* = 7.0, 3.9 Hz, 1H), 1.90 (d, *J* = 7.0 Hz, 3H), 1.88 – 1.80 (m, 1H), 1.80 – 1.69 (m, 3H), 1.69 – 1.59 (m, 1H), 1.37 – 1.21 (m, 2H), 1.21 – 0.92 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 46.7, 40.5, 32.1, 31.6, 26.4, 26.1, 26.0.

FT-IR (neat) 2981, 2925, 2852, 1448, 1377, 1295, 1236, 1196, 1164, 1145 cm^{-1}.

HRMS (GC) *m*/*z* $(M)^+$ calcd for $C_8H_{15}I$: 238.0219, found: 238.0194.



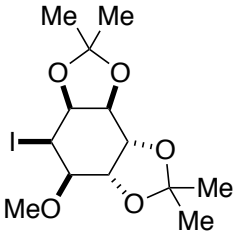
4-Iodotetrahydro-2*H*-thiopyran. The title compound was synthesized according to General Procedure A from tetrahydro-2*H*-thiopyran-4-ol[5] (2.00g, 16.9 mmol), PPh_3 (6.66 g, 25.4 mmol), imidazole (1.73 g, 25.4 mmol), and iodine (6.4 g, 25.4 mmol). The product was purified by flash chromatography with silica gel (hexanes). Colorless liquid; 1.80 g (47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.55 – 4.40 (m, 1H), 2.90 – 2.74 (m, 2H), 2.65 – 2.45 (m, 2H), 2.40 – 2.15 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 38.8, 31.0, 28.1.

FT-IR (neat) 2909, 2820, 1441, 1423, 1349, 1268, 1238, 1211, 1200, 1124, 990, 943, 905, 816, 671, 643 cm^{-1}.

HRMS (FAB) *m*/*z* $(M)^+$ calcd for C_5H_9IS: 227.9470, found: 227.9450.



(3a*S*,4*R*,5*R*,5a*S*,8a*R*,8b*S*)-4-Iodo-5-methoxy-2,2,7,7-tetramethylhexahydrobenzo[1,2-d:3,4-d']bis([1,3]dioxole). According to a literature procedure,[6] PPh_3 (1.39 g, 5.30 mmol) and imidazole (0.36 g, 5.30 mmol) were suspended in toluene (12 mL) at room temperature. Then, iodine (1.35 g, 5.30 mmol) was added slowly in portions, and the resulting mixture was stirred for 10 min. Next, 1,2:5,6-di-O-isopropylidene-D-chiro-inositol (1.00 g, 3.54 mmol) was added, and the resulting mixture was refluxed overnight. Then, the reaction mixture was allowed to cool to room temperature and poured into a mixture of CH_2Cl_2 (25 mL) and a saturated solution of $NaHCO_3$ (25 mL). After separation of the organic layer, the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were dried (Na_2SO_4), the solvent was removed in vacuo, and the residue was purified by flash chromatography with silica gel (2:1 hexanes/EtOAc). Crystalline solid; 1.19 g (89% yield, dr >20:1).

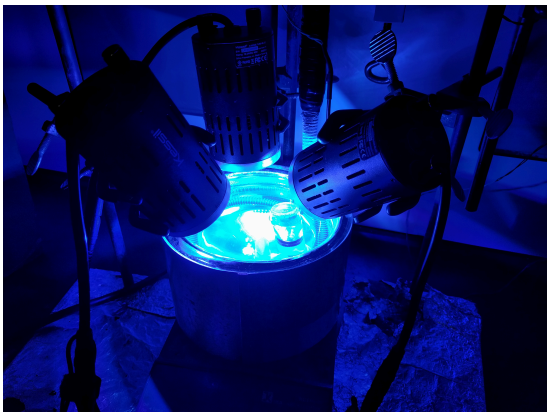
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (dd, *J* = 7.6, 4.7 Hz, 1H), 4.56 (dd, *J* = 5.0, 2.7 Hz, 1H), 4.46 (dd, *J* = 7.6, 4.4 Hz, 1H), 4.29 (dd, *J* = 8.0, 4.7 Hz, 1H), 4.18 (dd, *J* = 8.0, 5.0 Hz, 1H), 3.50 (s, 3H), 3.05 (dd, *J* = 4.4, 2.7 Hz, 1H), 1.60 (s, 3H), 1.47 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 110.2, 109.2, 81.2, 78.1, 77.4, 74.4, 73.7, 58.2, 29.4, 27.1, 26.0, 24.8, 24.3.

FT-IR (neat) 2992, 2932, 2892, 2830, 1746, 1455, 1372, 1250, 1212, 1167, 1097, 1073, 1053, 971 cm^{-1}.

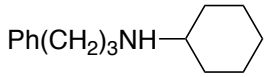
LRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{13}H_{22}IO_5$: 385.1, found: 385.0.

III. Photoinduced, Copper-Catalyzed N-Alkylations



General Procedure. CuI (6.7 mg, 0.035 mmol), *rac*-BINOL (20.1 mg, 0.070 mmol), and a stir bar were added to an oven-dried 20 mL vial. The vial was sealed with a septum cap, and then it was evacuated and backfilled with nitrogen (three cycles). DMF (1.0 mL), CH_3CN (4.0 mL), and BTPP (428 μL, 1.40 mmol) were added in turn. The mixture was stirred for 5 min, in order to dissolve the BTPP. Next, the amine (0.70 mmol) was added, followed by the alkyl iodide (1.05 mmol). The septum cap was covered with vacuum grease, the vial was detached from the Schlenk line, and the puncture holes were covered with vacuum grease. The vial was then placed upside down, freely moving, in an isopropanol bath cooled to −10 °C by an immersion cooler. The reaction mixture was stirred at −10 °C for 5 min, and then it was irradiated with three 34 W Kessil blue LED lamps, placed ~5 cm away, for 24 h. After the reaction was complete, the reaction mixture was transferred to a 250 mL round-bottom flask with the aid of CH_2Cl_2. Next, basic alumina was added to the flask, and then the solvent was removed by rotary evaporation and then placement under high vacuum, at which time a free-flowing powder was obtained. Products were visualized with a $KMnO_4$ stain on silica-gel TLC plates using solvent systems composed of hexane/EtOAc/7 N NH_3 in MeOH; traces of DMF and NEt_3 (used in purification) are usually visible after staining.

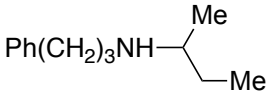
Protection as the Trifluoroacetamide Derivative. This procedure was used in two instances (Table 3, entries 4 and 6) to facilitate isolation and purification (volatility). After the reaction was complete, the grease was wiped from the septum cap, and the vial was placed under a positive pressure of nitrogen on a Schlenk line and allowed to warm to room temperature. Pyridine (310 μL, 3.85 mmol) and then trifluoroacetic anhydride (495 μL, 3.50 mmol) were added. After 10 min, the nitrogen inlet was removed, and the reaction mixture was stirred at room temperature for 3 h. Next, the reaction mixture was transferred to a 250 mL round-bottom flask with the aid of CH_2Cl_2, silica gel was added to the flask, and then the solvent was removed by rotary evaporation and then placement under high vacuum, at which time a free-flowing powder was obtained.



***N*-(3-Phenylpropyl)cyclohexanamine (Table 2, entry 1).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol). The product was purified by flash chromatography with basic alumina (8:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 122 mg (80% yield). Second run: 123 mg (80% yield).

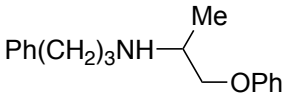
Gram Scale Reaction. CuI (143 mg, 0.750 mmol), *rac*-BINOL (429 mg, 1.50 mmol), and a cross-shaped stir bar were added to an oven-dried 100 mL round-bottom flask. The flask was sealed with a septum and then evacuated and backfilled with nitrogen (on a Schlenk line; three cycles). DMF (11.0 mL), CH_3CN (44.0 mL), and BTPP (4.59 mL, 15.0 mmol) were added in turn. The mixture was allowed to stir for 10 min, to solubilize the BTPP. Then, 3-phenylpropylamine (1.07 mL, 7.5 mmol) was added, followed by iodocyclohexane (1.46 mL, 11.3 mmol). The septum was covered with vacuum grease, the flask was detached from the Schlenk line, and the puncture holes were covered with vacuum grease. The flask was then fixed in an isopropanol bath cooled to −10 °C with an immersion cooler. The reaction mixture was stirred at −10 °C for 10 min, and then it was irradiated with four 34 W Kessil blue LED lamps, placed ~5 cm away, for 40 h. After the reaction was complete, the reaction mixture was transferred to a 500 mL round-bottom flask with the aid of CH_2Cl_2. Next, basic alumina was added to the flask, and then the solvent was removed by rotary evaporation and then placement under high vacuum, at which time a free-flowing powder was obtained. The residue was partially purified by flash chromatography with basic alumina (8:1:0.01 hexanes/EtOAc/NEt_3). The residue was then transferred to a 50 mL flask, concentrated, and placed under high vacuum for 4 h to remove traces of DMF. The residue was then purified by twice distilling with a Büchi Kugelrohr distillation apparatus (190 °C at 750 mTorr). Pale-yellow oil; 1.32 g (81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.21 (d, J = 7.0 Hz, 3H), 2.73 – 2.62 (m, 4H), 2.41 (tt, J = 10.5, 3.7 Hz, 1H), 1.93 – 1.79 (m, 4H), 1.79 – 1.69 (m, 2H), 1.69 – 1.59 (m, 1H), 1.47 (s, 1H), 1.32 – 1.13 (m, 3H), 1.12 – 1.01 (m, 2H). The ^{1}H NMR spectrum matches the spectrum reported in the literature.[7]



***N*-(3-Phenylpropyl)butan-2-amine (Table 2, entry 2).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and 2-iodobutane (124 μL, 1.05 mmol). The product was purified by flash chromatography with basic alumina (8:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 91 mg (68% yield). Second run: 95 mg (71% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.24 – 7.17 (m, 3H), 2.73 – 2.51 (m, 5H), 1.90 – 1.79 (m, 2H), 1.56 – 1.44 (m, 2H), 1.38 – 1.25 (m, 1H), 1.04 (d, *J* = 6.3 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). The ^{1}H NMR spectrum matches the spectrum reported in the literature.[8]



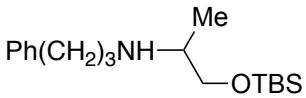
***N*-(1-Phenoxypropan-2-yl)-3-phenylpropan-1-amine (Table 2, entry 3).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and (2-iodopropoxy)benzene (276 mg, 1.05 mmol). The product was purified by flash chromatography with basic alumina (first column: 8:1:0.01 hexanes/EtOAc/NEt_3; second column: 3:1:0.01 hexanes/EtOAc/NEt_3 → 100% EtOAc). Pale-yellow oil. First run: 126 mg (67% yield). Second run: 119 mg (63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 4H), 7.23 – 7.09 (m, 3H), 7.03 – 6.81 (m, 3H), 3.87 (dd, *J* = 9.1, 4.6 Hz, 1H), 3.82 (dd, *J* = 9.1, 6.8 Hz, 1H), 3.15 – 3.03 (m, 1H), 2.80 – 2.59 (m, 4H), 1.95 – 1.71 (m, 2H), 1.56 (s, 1H), 1.15 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 142.2, 129.6, 128.42, 128.35, 125.9, 120.9, 114.7, 72.0, 52.5, 46.8, 33.8, 32.1, 17.6.

FR-IR (neat) 3026, 2925, 2858, 1599, 1586, 1495, 1454, 1371, 1337, 1299, 1170, 1078, 1036, 1001, 881, 813, 750, 711 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{24}NO$: 270.1852, found: 270.1852.



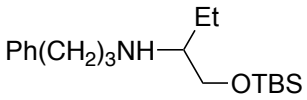
***N*-(1-((*tert*-Butyldimethylsilyl)oxy)propan-2-yl)-3-phenylpropan-1-amine (Table 2, entry 4).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and *tert*-butyl(2-iodopropoxy)dimethylsilane[9,10] (316 mg, 1.05 mmol). The product was purified by flash chromatography with basic alumina (8:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 157 mg (72% yield). Second run: 164 mg (76% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.16 (m, 3H), 3.59 – 3.38 (m, 2H), 2.80 – 2.65 (m, 4H), 2.59 (ddd, *J* = 11.2, 7.8, 6.6 Hz, 1H), 1.85 (qdd, *J* = 7.9, 6.4, 4.8 Hz, 2H), 1.63 (s, 1H), 0.99 (d, *J* = 6.4 Hz, 3H), 0.92 (s, 9H), 0.08 (d, *J* = 1.2 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 128.5, 128.5, 125.9, 67.5, 54.8, 46.9, 33.8, 32.2, 26.1, 18.4, 17.0, –5.2, –5.3.

FT-IR (neat) 3026, 2954, 2928, 2856, 1496, 1471, 1462, 1454, 1388, 1361, 1251, 1089, 1030, 1006, 842, 814, 774, 744, 697, 667 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{34}NOSi$: 308.2404, found: 308.2398.



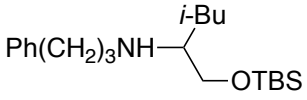
1-((*tert*-Butyldimethylsilyl)oxy)-*N*-(3-phenylpropyl)butan-2-amine (Table 2, entry 5). The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and *tert*-butyl(2-iodobutoxy)dimethylsilane (331 mg, 1.05 mmol). The product was purified by flash chromatography with basic alumina (8:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 127 mg (56% yield). Second run: 121 mg (54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.24 – 7.18 (m, 3H), 3.70 – 3.41 (m, 2H), 2.78 – 2.56 (m, 4H), 2.56 – 2.47 (m, 1H), 1.90 – 1.76 (m, 2H), 1.57 (s, 1H), 1.52 – 1.32 (m, 2H), 0.92 (d, *J* = 2.0 Hz, 12H), 0.08 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 128.5, 128.4, 125.8, 64.7, 60.8, 46.9, 33.8, 32.3, 26.1, 24.1, 18.4, 10.5, –5.2, –5.3.

FT-IR (neat) 3027, 2955, 2928, 2856, 1496, 1471, 1462, 1388, 1361, 1251, 1088, 1006, 938, 884, 813, 774, 743, 697, 668 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{19}H_{36}NOSi$: 322.2561, found: 322.2567.



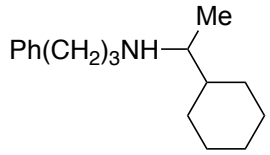
1-((*tert*-Butyldimethylsilyl)oxy)-4-methyl-*N*-(3-phenylpropyl)pentan-2-amine (Table 2, entry 6). The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and *tert*-butyl((2-iodo-4-methylpentyl)oxy)dimethyl-silane (361 mg, 1.05 mmol). The product was purified by flash chromatography with basic alumina (10:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 86 mg (35% yield). Second run: 33 mg (33% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.21 – 7.14 (m, 3H), 3.59 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.42 (dd, *J* = 10.0, 6.5 Hz, 1H), 2.75 – 2.44 (m, 5H), 1.86 – 1.75 (m, 2H), 1.71 – 1.55 (m, 1H), 1.48 (s, 1H), 1.30 – 1.12 (m, 2H), 1.01 – 0.74 (m, 15H), 0.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 128.5, 128.4, 125.8, 65.2, 57.3, 46.8, 41.2, 33.8, 32.3, 26.1, 25.2, 23.4, 23.0, 18.4, –5.2, –5.3.

FT-IR (neat) 3027, 2953, 2927, 2856, 1496, 1471, 1384, 1361, 1251, 1087, 1006, 936, 834, 812, 774, 743, 697, 668 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{21}H_{40}NOSi$: 350.2874, found: 350.2874.



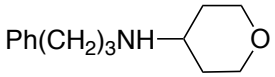
***N*-(1-Cyclohexylethyl)-3-phenylpropan-1-amine (Table 2, entry 7).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and (1-iodoethyl)cyclohexane (251 mg, 1.05 mmol). Catalyst loading: 10% CuI and 20% *rac*-BINOL. The product was purified by flash chromatography with basic alumina (10:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 72 mg (42% yield). Second run: 69 mg (40% yield). When enantiopure BINOL was used, the product was generated with <10% ee.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.14 – 7.07 (m, 3H), 2.66 – 2.54 (m, 3H), 2.47 (dt, *J* = 11.4, 7.2 Hz, 1H), 2.34 (qd, *J* = 6.5, 5.0 Hz, 1H), 1.77 – 1.63 (m, 4H), 1.63 – 1.54 (m, 3H), 1.29 – 0.97 (m, 5H), 0.96 – 0.83 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 128.5, 128.4, 125.8, 57.9, 47.2, 43.0, 33.9, 32.2, 30.1, 28.1, 26.9, 26.8, 26.6, 16.9.

FT-IR (neat) 3062, 3026, 2923, 2851, 1603, 1496, 1450, 1371, 1156, 1030, 745, 698 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{28}N$: 246.2216, found: 246.2218.



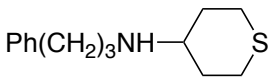
***N*-(3-Phenylpropyl)tetrahydro-2*H*-pyran-4-amine (Table 2, entry 8).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and 4-iodotetrahydro-2*H*-pyran (224 mg, 1.05 mmol). The product was purified by flash chromatography with basic alumina (3:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 129 mg (84% yield). Second run: 123 mg (80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 7.21 (dtd, *J* = 8.4, 3.3, 2.8, 1.8 Hz, 3H), 4.09 – 3.90 (m, 2H), 3.40 (td, *J* = 11.7, 2.2 Hz, 2H), 2.81 – 2.46 (m, 5H), 1.98 – 1.78 (m, 4H), 1.52 – 1.11 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 128.37, 128.36, 125.9, 67.0, 54.2, 46.1, 34.0, 33.8, 32.1.

FT-IR (neat) 3061, 2932, 2842, 1603, 1495, 1466, 1453, 1365, 1234, 1143, 1093, 1010, 981, 865, 817, 745, 712, 625 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{22}NO$: 220.1696, found: 220.1695.



***N*-(3-Phenylpropyl)tetrahydro-2*H*-thiopyran-4-amine (Table 2, entry 9).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine

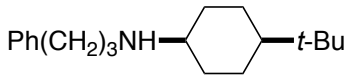
(99 μL, 0.70 mmol) and 4-iodotetrahydro-2*H*-thiopyran (240 mg, 1.05 mmol). Catalyst loading: 10% CuI and 20% *rac*-BINOL. The product was purified by flash chromatography with basic alumina (5:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 91 mg (55% yield). Second run: 93 mg (56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.21 (ddt, *J* = 8.1, 3.4, 1.5 Hz, 3H), 2.79 – 2.56 (m, 8H), 2.45 (tt, *J* = 10.3, 3.4 Hz, 1H), 2.20 – 2.11 (m, 2H), 1.83 (dtd, *J* = 9.0, 7.6, 6.6 Hz, 2H), 1.51 (dtd, *J* = 13.1, 10.2, 4.7 Hz, 2H), 0.91 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 128.38, 128.35, 125.9, 56.2, 46.3, 34.9, 33.8, 32.2, 27.8.

FT-IR (neat) 3052, 3018, 2903, 2850, 1606, 1493, 1450, 1423, 1338, 1272, 1218, 1200, 1124, 998, 948, 915, 815, 671 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{22}NS$: 236.1467, found: 236.1465.



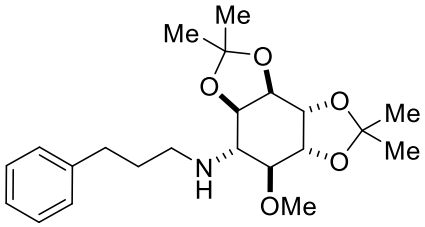
(1*R,4*R**)-4-(*tert*-Butyl)-*N*-(3-phenylpropyl)cyclohexan-1-amine (Table 2, entry 10).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and 1-(*tert*-butyl)-4-iodocyclohexane[11] (cis/trans 5:1; 281 mg, 1.05 mmol). The product was purified by flash chromatography with basic alumina (8:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 97 mg (51% yield, dr >20:1). Second run: 107 mg (56% yield, dr >20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 2.68 (ddd, *J* = 7.9, 6.8, 2.7 Hz, 4H), 2.39 – 2.29 (m, 1H), 2.01 – 1.92 (m, 2H), 1.90 – 1.66 (m, 5H), 1.10 – 0.98 (m, 5H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 128.5, 128.4, 125.9, 57.4, 48.0, 46.9, 34.2, 34.0, 32.5, 32.3, 27.8, 26.3.

FT-IR (neat) 3026, 2938, 2858, 1452, 1364, 745, 699 cm^{-1}.

HRMS (FAB) *m*/*z* $(M)^+$ calcd for $C_{19}H_{31}N$: 273.2457, found: 273.2467.



(3a*R*,4*S*,5*S*,5a*R*,8a*R*,8b*R*)-5-Methoxy-2,2,7,7-tetramethyl-*N*-(3-phenylpropyl)hexahydrobenzo[1,2-*d*:3,4-*d*']bis([1,3]dioxole)-4-amine (Table 2, entry 11). The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (161 μL, 0.70 mmol) and (3a*S*,4*R*,5*R*,5a*S*,8a*R*,8b*S*)-4-iodo-5-methoxy-2,2,7,7-

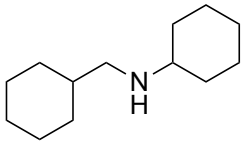
tetramethylhexahydrobenzo[1,2-*d*:3,4-*d*']bis([1,3]dioxole) (β/α >20:1; 269 mg, 0.70 mmol). Catalyst loading: 10% CuI and 20% *rac*-BINOL; reaction time: 48 h. The product was purified by flash chromatography with basic alumina (10:1:0.01 → 5:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 170 mg (62% yield, dr >20:1). Second run: 165 mg (60% yield, dr >20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.25 – 7.17 (m, 3H), 4.26 – 4.16 (m, 2H), 4.16 – 4.06 (m, 2H), 3.55 (s, 3H), 3.22 (dd, *J* = 11.7, 6.3 Hz, 1H), 2.93 – 2.84 (m, 1H), 2.78 – 2.63 (m, 4H), 1.98 (s, 1H), 1.91 – 1.80 (m, 2H), 1.53 (s, 3H), 1.51 (s, 3H), 1.37 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 128.5, 128.4, 125.8, 110.0, 109.9, 80.3, 80.2, 80.0, 77.6, 77.2, 59.4, 59.0, 47.6, 33.7, 32.1, 28.0, 27.9, 25.5, 25.4.

FT-IR (neat) 3328, 2986, 2934, 1603, 1496, 1454, 1380, 1370, 1245, 1214, 1160, 1110, 1090, 976 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{22}H_{34}NO_5$: 392.2431, found: 392.2441.



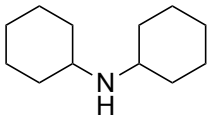
***N*-(Cyclohexylmethyl)cyclohexanamine (Table 3, entry 1).** The title compound was synthesized according to the General Procedure from cyclohexanemethylamine (91 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol) using 10% CuI (13.3 mg, 0.070 mmol) and 20% *rac*-BINOL (40.1 mg, 0.140 mmol). The product was purified by flash chromatography with basic alumina (12:1:0.01 → 6:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 112 mg (82% yield). Second run: 115 mg (84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (d, *J* = 6.7 Hz, 2H), 2.42 – 2.32 (m, 1H), 1.94 – 1.83 (m, 2H), 1.78 – 1.59 (m, 8H), 1.49 – 1.37 (m, 1H), 1.31 – 1.00 (m, 9H), 0.97 – 0.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 56.9, 53.8, 38.2, 33.7, 31.6, 26.7, 26.2, 26.1, 25.2.

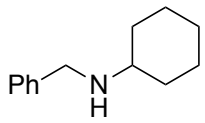
FT-IR (neat) 2922, 2851, 1448, 1129 cm^{-1}.

HRMS (FAB) *m*/*z* $(M+H)^+$ calcd for $C_{13}H_{26}N$: 196.2065, found: 196.2067.



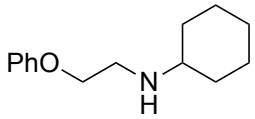
Dicyclohexylamine (Table 3, entry 2). The title compound was synthesized according to the General Procedure from cyclohexylamine (80 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol) using 10% CuI (13.3 mg, 0.070 mmol) and 20% *rac*-BINOL (40.1 mg, 0.140 mmol). The product was purified by flash chromatography with basic alumina (15:1:0.01 → 6:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 93 mg (73% yield). Second run: 88 mg (69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.56 (tt, *J* = 10.6, 3.8 Hz, 2H), 1.87 (ddt, *J* = 15.1, 6.3, 2.8 Hz, 4H), 1.80 – 1.67 (m, 4H), 1.62 (dpd, *J* = 12.1, 3.3, 1.5 Hz, 2H), 1.32 – 1.10 (m, 6H), 1.09 – 0.97 (m, 4H), 0.86 (s, 1H). The ^{1}H NMR spectrum matches the spectrum reported in the literature.[12]



***N*-Benzylcyclohexanamine (Table 3, entry 3).** The title compound was synthesized according to the General Procedure from benzylamine (76 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol). The product was purified by flash chromatography with basic alumina (12:1:0.01 → 5:1:0.01 hexanes/EtOAc/NEt_3). Pale-red oil. First run: 98 mg (74% yield). Second run: 89 mg (67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 4.4 Hz, 4H), 7.20 – 7.14 (m, 1H), 3.74 (s, 2H), 2.42 (tt, *J* = 10.2, 3.7 Hz, 1H), 1.89 – 1.80 (m, 2H), 1.66 (dt, *J* = 12.4, 3.5 Hz, 2H), 1.54 (dtd, *J* = 10.4, 3.3, 1.8 Hz, 1H), 1.38 – 1.26 (m, 1H), 1.22 – 1.00 (m, 5H). The ^{1}H NMR spectrum matches the spectrum reported in the literature.[13]



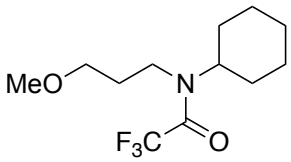
***N*-(2-Phenoxyethyl)cyclohexanamine (Table 3, entry 4).** The title compound was synthesized according to the General Procedure from 2-phenoxyethylamine (92 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol) using 10% CuI (13.3 mg, 0.070 mmol) and 20% *rac*-BINOL (40.1 mg, 0.140 mmol). The product was purified by flash chromatography with basic alumina (first column: 8:1:0.01 hexanes/EtOAc/NEt_3; second column: 3:1:0.01 → 0:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 94 mg (61% yield). Second run: 94 mg (61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.25 (m, 2H), 7.01 – 6.90 (m, 3H), 4.09 (t, *J* = 5.3 Hz, 2H), 3.05 (t, *J* = 5.3 Hz, 2H), 2.51 (tt, *J* = 10.5, 3.8 Hz, 1H), 2.00 – 1.90 (m, 2H), 1.85 – 1.73 (m, 2H), 1.70 – 1.61 (m, 1H), 1.58 (s, 1H), 1.34 – 1.08 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 129.6, 120.9, 114.7, 67.7, 56.8, 46.1, 33.7, 26.3, 25.2.

FT-IR (neat) 2924, 2851, 1599, 1587, 1496, 1458, 1242, 1171, 1135, 1079, 1042, 883, 800, 751, 690 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{22}NO$: 220.1696, found: 220.1693.



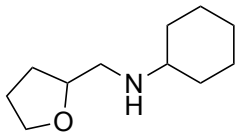
***N*-Cyclohexyl-2,2,2-trifluoro-*N*-(3-methoxypropyl)acetamide (Table 3, entry 5).** The title compound was synthesized according to the General Procedure from 3-methoxypropylamine (76 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol) using 10% CuI (13.3 mg, 0.070 mmol) and 20% *rac*-BINOL (40.1 mg, 0.140 mmol). The reaction mixture was then subjected to in situ protection. The product was purified by flash chromatography with silica gel (95:5 → 80:20 hexanes/EtOAc). Pale-yellow oil. First run: 151 mg (81% yield). Second run: 163 mg (87% yield).

^{1}H NMR (500 MHz, d$_6$-DMSO, 130 °C) δ 3.77 – 3.65 (m, 1H), 3.41 (s, 4H), 3.28 (d, *J* = 4.8 Hz, 3H), 1.83 (q, *J* = 6.8 Hz, 4H), 1.77 – 1.59 (m, 5H), 1.42 – 1.27 (m, 2H), 1.19 (td, *J* = 12.6, 5.9 Hz, 1H).

^{13}C NMR (126 MHz, d$_6$-DMSO, 130 °C) δ 156.2 (q, *J* = 34.6 Hz), 117.1 (q, *J* = 288.7 Hz), 70.1, 58.4, 58.2, 41.9, 30.8, 29.6, 25.8, 25.1.

FT-IR (neat) 2934, 2860, 1682, 1447, 1257, 1207, 1184, 1117, 1030, 998, 896, 758, 705 cm^{-1}.

HRMS (ESI) *m*/*z* (M+H)$^+$ calcd for $C_{12}H_{21}F_3NO_2$: 268.1519, found: 268.1503.



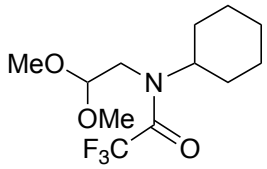
***N*-((Tetrahydrofuran-2-yl)methyl)cyclohexanamine (Table 3, entry 6).** The title compound was synthesized according to the General Procedure from tetrahydrofurfurylamine (72 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol) using 10% CuI (13.3 mg, 0.070 mmol) and 20% *rac*-BINOL (40.1 mg, 0.140 mmol). The product was purified by flash chromatography with basic alumina (3:1:0.01 → 1:1:0.01 hexanes/EtOAc/NEt$_3$). Pale-yellow oil. First run: 77 mg (60% yield). Second run: 76 mg (59% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 3.99 (dtd, *J* = 7.7, 6.9, 3.7 Hz, 1H), 3.86 (dt, *J* = 8.3, 6.6 Hz, 1H), 3.76 (dt, *J* = 8.2, 6.8 Hz, 1H), 2.75 (dd, *J* = 11.7, 3.8 Hz, 1H), 2.64 (dd, *J* = 11.8, 8.1 Hz, 1H), 2.43 (tt, *J* = 10.4, 3.8 Hz, 1H), 2.01 – 1.86 (m, 5H), 1.74 (dt, *J* = 13.2, 3.9 Hz, 2H), 1.65 – 1.48 (m, 3H), 1.30 – 1.06 (m, 5H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 78.6, 67.8, 57.0, 51.7, 33.6, 33.5, 29.4, 26.2, 25.7, 25.09, 25.07.

FT-IR (neat) 2923, 2851, 1673, 1449, 1368, 1258, 1183, 1139, 1068, 1018, 919, 889, 843, 788, 742 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* (M+H)$^+$ calcd for $C_{11}H_{22}NO$: 184.1696, found: 184.1698.



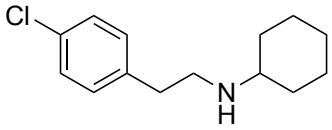
***N*-Cyclohexyl-*N*-(2,2-dimethoxyethyl)-2,2,2-trifluoroacetamide (Table 3, entry 7).** The title compound was synthesized according to the General Procedure from 2,2-dimethoxyethylamine (76 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol) using 10% CuI (13.3 mg, 0.070 mmol) and 20% *rac*-BINOL (40.1 mg, 0.140 mmol). The reaction mixture was then subjected to in situ protection. The product was purified by flash chromatography with silica gel (95:5 → 80:20 hexanes/EtOAc). Pale-yellow oil. First run: 147 mg (74% yield). Second run: 150 mg (76% yield).

^{1}H NMR (500 MHz, d$_6$-DMSO, 100 °C) δ 4.56 (t, *J* = 4.9 Hz, 1H), 3.64 (p, *J* = 7.5 Hz, 1H), 3.43 (d, *J* = 5.0 Hz, 2H), 3.35 (d, *J* = 2.0 Hz, 6H), 1.81 (d, *J* = 13.5 Hz, 2H), 1.77 – 1.66 (m, 4H), 1.61 (dt, *J* = 13.2, 3.2 Hz, 1H), 1.34 – 1.23 (m, 2H), 1.15 (ddt, *J* = 16.3, 12.9, 6.5 Hz, 1H).

^{13}C NMR (126 MHz, d$_6$-DMSO, 100 °C) δ 156.7 (d, *J* = 34.3 Hz), 117.0 (d, *J* = 289.1 Hz), 102.9, 58.7, 55.2, 47.0, 30.9, 25.9, 25.1.

FT-IR (neat) 2936, 2858, 1684, 1447, 1257, 1211, 1187, 1137, 1122, 1077, 1032, 981, 896, 809, 759, 711 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* (M+H)$^+$ calcd for $C_{12}H_{21}F_3NO_3$: 284.1468, found: 284.1494.



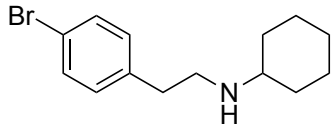
***N*-(4-Chlorophenethyl)cyclohexanamine (Table 3, entry 8).** The title compound was synthesized according to the General Procedure from 4-chlorophenethylamine (98 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol) using 10% CuI (13.3 mg, 0.070 mmol) and 20% *rac*-BINOL (40.1 mg, 0.140 mmol). The product was purified by flash chromatography with basic alumina (3:1:0.01 → 1:1:0.01 hexanes/EtOAc/NEt$_3$). Pale-yellow oil. First run: 102 mg (61% yield). Second run: 111 mg (67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.18 – 7.13 (m, 2H), 2.97 – 2.74 (m, 4H), 2.44 (tt, *J* = 10.5, 3.8 Hz, 1H), 1.93 – 1.81 (m, 2H), 1.79 – 1.68 (m, 2H), 1.67 – 1.57 (m, 1H), 1.32 – 1.03 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 131.8, 130.0, 128.5, 56.8, 48.1, 36.0, 33.6, 26.1, 25.1.

FT-IR (neat) 2924, 2851, 1491, 1448, 1406, 1363, 1347, 1125, 1091, 1015, 889, 834, 809, 714, 667, 630 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* (M+H)$^+$ calcd for $C_{14}H_{21}ClN$: 238.1357, found: 238.1352.



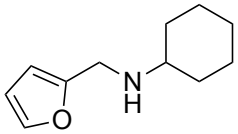
***N*-(4-Bromophenethyl)cyclohexanamine (Table 3, entry 9).** The title compound was synthesized according to the General Procedure from 4-bromophenethylamine (109 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol). The product was purified by flash chromatography with basic alumina (3:1:0.01 → 1:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 103 mg (52% yield). Second run: 104 mg (53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2H), 7.16 – 7.07 (m, 2H), 2.97 – 2.86 (m, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.43 (tt, *J* = 10.5, 3.8 Hz, 1H), 1.92 – 1.84 (m, 2H), 1.73 (dt, *J* = 13.4, 3.7 Hz, 2H), 1.66 – 1.59 (m, 1H), 1.36 – 1.12 (m, 4H), 1.11 – 1.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 131.5, 130.4, 119.9, 56.7, 48.0, 36.1, 33.6, 26.1, 25.1.

FT-IR (neat) 2930, 2853, 1488, 1449, 1127, 1072, 1011, 808 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{21}{}^{79}BrN$: 282.0852, found: 282.0849.



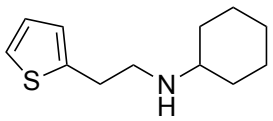
***N*-(Furan-2-ylmethyl)cyclohexanamine (Table 3, entry 10).** The title compound was synthesized according to the General Procedure from furfurylamine (72 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol). The product was purified by flash chromatography with basic alumina (6:1:0.01 → 1:2:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 64 mg (55% yield). Second run: 64 mg (52% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.17 – 6.10 (m, 1H), 3.80 (d, *J* = 0.7 Hz, 2H), 2.44 (tt, *J* = 10.4, 3.8 Hz, 1H), 1.94 – 1.82 (m, 2H), 1.76 – 1.67 (m, 2H), 1.64 – 1.54 (m, 1H), 1.40 (s, 1H), 1.29 – 1.07 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 141.6, 110.1, 106.5, 55.8, 43.4, 33.4, 26.1, 25.0.

FT-IR (neat) 2924, 2852, 1505, 1449, 1370, 1345, 1147, 1117, 1074, 1010, 919, 885, 803, 727 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{11}H_{18}NO$: 180.1383, found: 180.1382.



***N*-(2-(Thiophen-2-yl)ethyl)cyclohexanamine (Table 3, entry 11).** The title compound was synthesized according to the General Procedure from thiophene-2-ethylamine (82 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol) using 10% CuI (13.3 mg, 0.070 mmol) and 20% *rac*-BINOL (40.1 mg, 0.140 mmol). The product was purified by flash

chromatography with basic alumina (6:1:0.01 → 1:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 117 mg (80% yield). Second run: 117 mg (80% yield).

^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.84 (dt, *J* = 3.5, 1.1 Hz, 1H), 3.06 – 2.87 (m, 4H), 2.44 (tt, *J* = 10.5, 3.8 Hz, 1H), 1.91 – 1.81 (m, 2H), 1.76 – 1.67 (m, 2H), 1.66 – 1.57 (m, 1H), 1.28 – 1.01 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 126.8, 124.9, 123.5, 56.6, 48.3, 33.6, 30.8, 26.2, 25.1.

FT-IR (neat) 2923, 2850, 1447, 1364, 1258, 1126, 1041, 889, 848, 820, 689 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{12}H_{20}NS$: 210.1311, found: 210.1310.

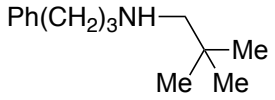
IV. Reactions with Neopentyl Iodide (eq 5)

In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with a stir bar and, when applicable, CuI (3.8 mg, 0.020 mmol) and *rac*-BINOL (11.5 mg, 0.0400 mmol). DMF (0.3 mL), CH_3CN (1.1 mL), and BTPP (122 μL, 0.400 mmol) were added in turn. The reaction mixture was allowed to stir for 5 min, to solubilize the BTPP. Then, 3-phenylpropylamine (28.5 μL, 0.200 mmol) was added, followed by neopentyl iodide (40 μL, 0.30 mmol). The vial was immediately sealed with a PTFE-lined vial cap and then removed from the glovebox.

Entries 1 and 2: The vial was placed upside-down in a fixed position in an isopropanol bath cooled to −10 °C with an immersion cooler. The reaction mixture was stirred at −10 °C for 5 min, and then, if applicable, it was irradiated with a single 34 W Kessil blue LED lamp from ~3 cm away for 24 h.

Entries 3 and 4: The vial was placed in a 100 °C oil bath for 24 h.

^{1}H NMR analysis. A 20 mL vial was charged with a known amount of 1,3,5-trimethoxybenzene. The reaction vessel was uncapped, diluted with CH_2Cl_2 (~2 mL), recapped, and shaken. Then, the mixture was passed through a plug of basic alumina into the 20 mL vial containing the internal standard. The reaction vessel was washed three times with EtOAc (~4 mL), and the washings were passed through a plug of basic alumina into the 20 mL vial. The filtered reaction mixture was concentrated and then placed under high vacuum for 2 h in order to remove most of the DMF.



2,2-Dimethyl-*N*-(3-phenylpropyl)propan-1-amine. The title compound was synthesized according to the General Procedure (see Section III) from 3-phenylpropylamine (99 μL, 0.70 mmol) and 1-iodo-2,2-dimethylpropane (140 μL, 1.05 mmol). Catalyst loading: 10% CuI and 20% *rac*-BINOL; reaction time: 48 h. The product was purified by flash chromatography with basic alumina (8:1:0.01 hexanes/EtOAc/NEt_3). Pale-yellow oil. First run: 101 mg (70% yield). Second run: 99 mg (69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.26 – 7.17 (m, 3H), 2.74 – 2.62 (m, 4H), 2.36 (s, 2H), 1.91 – 1.79 (m, 2H), 0.93 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 128.5, 128.4, 125.8, 62.5, 50.6, 33.8, 31.8, 31.5, 28.0.

FT-IR (neat) 3026, 2949, 2863, 2809, 1496, 1463, 1453, 1361, 1125, 1030, 907, 742, 710 cm^{-1}.

HRMS (ESI/APCI) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{24}N$: 206.1903, found: 206.1896.

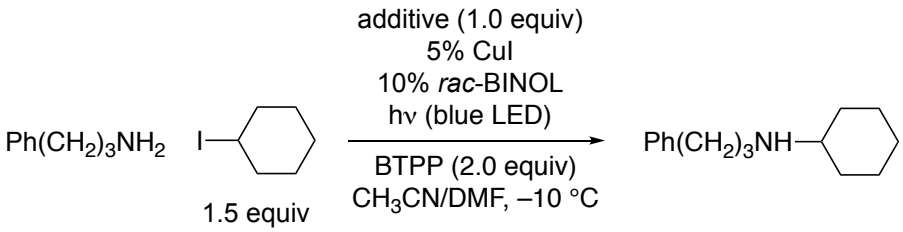
V. TEMPO Trapping Experiment (eq 6)

In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with CuI (1.9 mg, 0.010 mmol), *rac*-BINOL (5.7 mg, 0.020 mmol), and a stir bar. DMF (0.3 mL), CH_3CN (1.1 mL), and BTPP (122 μL, 0.400 mmol) were added in turn. The reaction mixture was allowed to stir for 5 min, to solubilize the BTPP. Then, 3-phenylpropylamine (28.5 μL, 0.200 mmol) was added, followed by iodocyclohexane (39.0 μL, 0.302 mmol) and TEMPO (47 mg, 0.30 mmol). Next, the vial was immediately sealed with a PTFE-lined vial cap, removed from the glovebox, and placed upside-down in a fixed position in an isopropanol bath cooled to −10 °C with an immersion cooler. After stirring for 5 min at −10 °C, the reaction mixture was irradiated with a single 34 W Kessil blue LED lamp, placed ~3 cm away, for 24 h. The experiment was run four times: twice for GC analysis (to determine the yield of the TEMPO adduct) and twice for ^{1}H NMR analysis (to determine the yield of the product).

GC analysis. Tetradecane (52.0 μL, 0.200 mmol) was added to the reaction mixture, and then the mixture was diluted with CH_2Cl_2 (~2 mL). An aliquot (~200 μL) of the reaction mixture was passed through a plug of silica gel, followed by EtOAc (~1 mL). The filtrate was then analyzed by GC.

^{1}H NMR analysis. A 20 mL vial was charged with a known amount of 1,3,5-trimethoxybenzene. The reaction vessel was uncapped, diluted with CH_2Cl_2 (~2 mL), recapped, and shaken. Then, the mixture was passed through a plug of basic alumina into the 20 mL vial containing the internal standard. The reaction vessel was washed three times with EtOAc (~4 mL), and the washings were passed through a plug of basic alumina into the 20 mL vial. The filtered reaction mixture was concentrated and then placed under high vacuum for 2 h in order to remove most of the DMF.

VI. Effect of Additives



In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with CuI (1.9 mg, 0.010 mmol), *rac*-BINOL (5.7 mg, 0.020 mmol), and a stir bar. DMF (0.3 mL), CH_3CN (1.1 mL), and BTPP (122 μL, 0.400 mmol) were added in turn. The reaction mixture was allowed to stir for 5 min, to solubilize the BTPP. Then, 3-phenylpropylamine (28.5 μL, 0.200 mmol) was added, followed by iodocyclohexane (39.0 μL, 0.302 mmol) and the additive (0.200 mmol). Next, the vial was immediately sealed with a PTFE-lined vial cap, removed from the glovebox, and placed upside-down in a fixed position in an isopropanol bath cooled to −10 °C with an immersion cooler. After stirring for 5 min at −10 °C, the reaction mixture was irradiated with a single 34 W Kessil blue LED lamp, placed ~3 cm away, for 24 h. For each additive, four reactions were run: two for GC analysis (to determine the amount of additive remaining) and two for ^{1}H NMR analysis (to determine the yield of the product).

GC analysis. Tetradecane (52.0 μL, 0.200 mmol) was added to the reaction mixture, and then the mixture was diluted with CH_2Cl_2 (~2 mL). An aliquot (~200 μL) of the reaction mixture was passed through a plug of silica gel, followed by EtOAc (~1 mL). The filtrate was then analyzed by GC.

^{1}H NMR analysis. A 20 mL vial was charged with a known amount of 1,3,5-trimethoxybenzene. The reaction vessel was uncapped, diluted with CH_2Cl_2 (~2 mL), recapped, and shaken. Then, the mixture was passed through a plug of basic alumina into the 20 mL vial containing the internal standard. The reaction vessel was washed three times with EtOAc (~4 mL), and the washings were passed through a plug of basic alumina into the 20 mL vial. The filtered reaction mixture was concentrated and then placed under high vacuum for 2 h in order to remove most of the DMF.

Table S1. Effect of additives (average of two experiments).

Entry	Additive	Remaining Additive (%)	Yield(%)
1	*cis*-5-decene	97	92
2	*trans*-5-decene	95	92
3	5-nonanol	92	90
4	5-decyne	97	87
5	methyl octanoate	98	84
6	2-nonanone	>99	78
7	iodobenzene	61	100

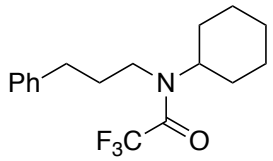
8	*N*-methylpyrrolidone	99	90
9	pyridine	88	66
10	cyclohexanecarboxaldehyde	44	51
11	nitrocyclopentane	–	<1

VII. N-Protection of the Amine

The yields have not been optimized.

Table S2. N-Protection of the Amine.

Entry	Protecting Group	Yield(%)
1	Trifluoroacetamide	86
2	Boc	73
3	Troc	68
4	Tosyl	64
5	Nosyl	56



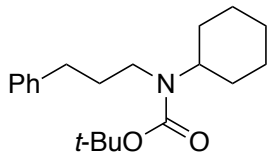
***N*-Cyclohexyl-2,2,2-trifluoro-*N*-(3-phenylpropyl)acetamide (Table S2, entry 1).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol). After the N-alkylation was complete, the reaction mixture was allowed to warm to room temperature. Next, pyridine (310 μL, 3.87 mmol) and TFAA (500 μL, 3.51 mmol) were added, and the resulting mixture was stirred at room temperature for 5 h. Then, the reaction mixture was transferred to a 250 mL round-bottom flask with the aid of CH_2Cl_2, silica gel was added to the flask, and the solvent was removed by rotary evaporation. The product was purified by flash chromatography with silica gel (90:10 → 50:50 hexanes/Et_2O). Colorless oil. First run: 188 mg (86% yield). Second run: 189 mg (86% yield).

^{1}H NMR (500 MHz, d_6-DMSO, 130 °C) δ 7.29 (t, *J* = 7.7 Hz, 2H), 7.25 – 7.16 (m, 3H), 3.70 (td, *J* = 11.6, 5.4 Hz, 1H), 3.43 – 3.27 (m, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 1.91 (t, *J* = 7.8 Hz, 2H), 1.81 (dt, *J* = 13.4, 3.5 Hz, 2H), 1.75 – 1.50 (m, 5H), 1.38 – 1.26 (m, 2H), 1.21 – 1.08 (m, 1H).

^{13}C NMR (126 MHz, d_6-DMSO, 130 °C) δ 156.1 (q, *J* = 34.3 Hz), 141.5, 128.7, 128.6, 126.2, 117.1 (q, *J* = 288.8 Hz), 58.3, 44.1, 33.1, 30.8, 25.8, 25.1.

FT-IR (neat) 2935, 2859, 1679, 1497, 1453, 1257, 1207, 1181, 1132, 1084, 1030, 996, 896, 749, 698 cm^{-1}.

LRMS (ESI) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{23}F_3NO$: 314.2, found: 314.1.



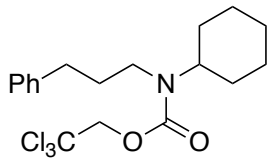
***tert*-Butyl cyclohexyl(3-phenylpropyl)carbamate (Table S2, entry 2).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol). After the N-alkylation was complete, the reaction mixture was allowed to warm to room temperature. Next, Boc_2O (764 mg, 3.50 mmol) and 4-DMAP (86 mg, 0.70 mmol) were added, and the resulting mixture was stirred at room temperature for 24 h. Then, the reaction mixture was transferred to a 250 mL round-bottom flask with the aid of CH_2Cl_2, silica gel was added to the flask, and the solvent was removed by rotary evaporation. The product was purified by flash chromatography with silica gel (95:5 → 50:50 hexanes/Et_2O). Colorless oil. First run: 162 mg (73% yield). Second run: 161 mg (73% yield).

^{1}H NMR (500 MHz, d_6-DMSO, 70 °C) δ 7.27 (dd, *J* = 7.9, 7.1 Hz, 2H), 7.22 – 7.13 (m, 3H), 3.60 (s, 1H), 3.11 – 3.04 (m, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.82 – 1.69 (m, 4H), 1.65 – 1.54 (m, 3H), 1.48 – 1.39 (m, 2H), 1.38 (s, 9H), 1.24 (qt, *J* = 13.1, 3.6 Hz, 2H), 1.04 (qt, *J* = 13.0, 3.7 Hz, 1H).

^{13}C NMR (126 MHz, d_6-DMSO, 70 °C) δ 154.9, 142.2, 128.65, 128.57, 126.1, 78.6, 56.0, 43.4, 33.3, 32.3, 31.2, 28.6, 26.2, 25.6.

FT-IR (neat) 2973, 2930, 2856, 1720, 1687, 1497, 1453, 1410, 1390, 1364, 1298, 1273, 1254, 1159, 1101, 1076, 908, 894, 869, 774, 749, 698 cm^{-1}.

HRMS (FAB) *m*/*z* $(M+H)^+$ calcd for $C_{20}H_{32}NO_2$: 318.2433, found: 318.2433.



2,2,2-Trichloroethyl cyclohexyl(3-phenylpropyl)carbamate (Table S2, entry 3). The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol). After the N-alkylation was complete, the reaction mixture was allowed to warm to room temperature. Next, pyridine (310 μL, 3.87 mmol) and TrocCl (742 mg, 3.50 mmol) were added, and the resulting mixture was stirred at room temperature for 24 h. Then, the reaction mixture was transferred to a 250 mL round-bottom flask with the aid of CH_2Cl_2, silica gel was added to the flask, and the solvent was removed by rotary evaporation. The product was purified by flash chromatography with silica gel (95:5 → 50:50 hexanes/Et_2O). Pale-yellow oil. First run: 193 mg (70% yield). Second run: 180 mg (65% yield).

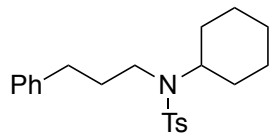
^{1}H NMR (500 MHz, d_6-DMSO, 100 °C) δ 7.30 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 4.82 (s, 2H), 3.69 (tt, *J* = 12.0, 3.8 Hz, 1H), 3.26 (ddd, *J* = 9.6, 6.8, 1.6 Hz, 2H), 2.62 (t, *J* = 7.8 Hz, 2H), 1.89 (t, *J* =

7.6 Hz, 2H), 1.80 – 1.67 (m, 4H), 1.64 – 1.49 (m, 3H), 1.36 – 1.22 (m, 2H), 1.10 (ddt, *J* = 16.8, 13.1, 6.5 Hz, 1H).

^{13}C NMR (126 MHz, d_6-DMSO, 100 °C) δ 153.9, 142.0, 128.65, 128.57, 126.1, 96.8, 74.8, 57.4, 44.3, 33.2, 31.7, 31.0, 26.1, 25.4.

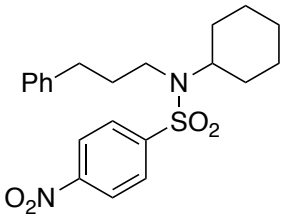
FT-IR (neat) 2931, 2855, 1712, 1471, 1452, 1418, 1297, 1242, 1168, 1119, 1058, 761, 750, 719, 699 cm^{-1}.

LRMS (ESI) *m*/*z* (M+H)$^+$ calcd for $C_{18}H_{25}Cl_3NO_2$: 392.1, found: 392.1.



***N*-Cyclohexyl-4-methyl-*N*-(3-phenylpropyl)benzenesulfonamide (Table S2, entry 4).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol). After the N-alkylation was complete, the reaction mixture was allowed to warm to room temperature. Next, CH_2Cl_2 (5 mL), aqueous NaOH (2 N, 2.5 mL), and TsCl (666 mg, 3.50 mmol) were added, and the resulting mixture was stirred at room temperature for 18 h. Then, the reaction mixture was transferred to a 250 mL round-bottom flask with the aid of CH_2Cl_2, silica gel was added to the flask, and the solvent was removed by rotary evaporation. The product was purified by flash chromatography with silica gel (100:0 → 75:25 hexanes/EtOAc). White solid. First run: 163 mg (63% yield). Second run: 167 mg (64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 2H), 7.31 – 7.24 (m, 4H), 7.22 – 7.16 (m, 3H), 3.61 (tt, *J* = 11.3, 3.5 Hz, 1H), 3.18 – 3.04 (m, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 2.41 (s, 3H), 2.08 – 1.90 (m, 2H), 1.70 (d, *J* = 8.7 Hz, 2H), 1.63 – 1.51 (m, 4H), 1.36 – 1.16 (m, 4H). The ^{1}H NMR spectrum matches the spectrum reported in the literature.[14]



***N*-Cyclohexyl-4-nitro-*N*-(3-phenylpropyl)benzenesulfonamide (Table S2, entry 5).** The title compound was synthesized according to the General Procedure from 3-phenylpropylamine (99 μL, 0.70 mmol) and iodocyclohexane (136 μL, 1.05 mmol). After the N-alkylation was complete, the reaction mixture was allowed to warm to room temperature. Next, CH_2Cl_2 (5 mL), NEt_3 (540 μL, 3.87 mmol), and 4-nitrobenzenesulfonyl chloride (708 mg, 3.50 mmol) were added, and the resulting mixture was stirred at room temperature for 18 h.

Then, the reaction mixture was transferred to a 250 mL round-bottom flask with the aid of CH_2Cl_2, silica gel was added to the flask, and the solvent was removed by rotary evaporation. The product was purified by flash chromatography with silica gel (100:0 → 75:25 hexanes/EtOAc). White solid. First run: 154 mg (55% yield). Second run: 158 mg (56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 – 8.28 (m, 2H), 7.98 – 7.89 (m, 2H), 7.33 – 7.28 (m, 2H), 7.24 – 7.15 (m, 3H), 3.74 – 3.55 (m, 1H), 3.20 – 3.08 (m, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.07 – 1.93 (m, 2H), 1.82 – 1.71 (m, 2H), 1.60 (d, *J* = 15.6 Hz, 4H), 1.26 (q, *J* = 10.5, 9.3 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 147.5, 141.0, 128.6, 128.5, 128.1, 126.3, 124.4, 58.7, 43.8, 33.21, 33.16, 32.0, 26.1, 25.3.

FT-IR (neat) 2932, 2858, 1603, 1524, 1495, 1469, 1451, 1340, 1322, 1306, 1280, 1211, 1169, 1153, 1121, 1086, 1055, 1029, 1013, 982, 896, 821, 750, 742, 733, 700, 615 cm^{-1}.

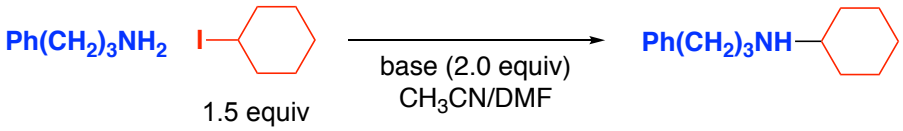
LRMS (ESI) *m*/*z* $(M+H)^+$ calcd for $C_{21}H_{27}N_2O_4S$: 403.2, found: 403.1.

VIII. Data on S_N2 Reactions

In a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with base (when LiO*t*-Bu or KH was used as base; 0.400 mmol) and a stir bar. DMF (0.3 mL), CH_3CN (1.1 mL), and base (when BTPP was used as base; 0.400 mmol) were added in turn. The reaction mixture was allowed to stir for 5 min to solubilize the base. Then, 3-phenylpropylamine (28.5 μL, 0.200 mmol) was added, followed by iodocyclohexane (39.0 μL, 0.302 mmol). The base-free reactions used an excess of 3-phenylpropylamine (57.0 μL, 0.401 mmol) relative to iodocyclohexane (26.0 μL, 0.201 mmol). Next, the vial was immediately sealed with a PTFE-lined vial cap, removed from the glovebox, and stirred at the indicated temperature for 24 h. For each reaction at each temperature, four reactions were run: two for GC analysis (to determine the amount of remaining electrophile) and two for ^{1}H NMR analysis (to determine the yield of the product).

GC analysis. Tetradecane (52.0 μL, 0.200 mmol) was added to the reaction mixture, and then the mixture was diluted with CH_2Cl_2 (~2 mL). An aliquot (~200 μL) of the reaction mixture was passed through a plug of silica gel, followed by EtOAc (~1 mL). The filtrate was then analyzed by GC.

^{1}H NMR analysis. A 20 mL vial was charged with a known amount of 1,3,5-trimethoxybenzene. The reaction vessel was uncapped, diluted with CH_2Cl_2 (~2 mL), re-capped, and shaken. Then, the mixture was passed through a plug of basic alumina into the 20 mL vial containing the internal standard. The reaction vessel was washed three times with EtOAc (~4 mL), and the washings were passed through a plug of basic alumina into the 20 mL vial. The filtered reaction mixture was concentrated and then placed under high vacuum for 2 h in order to remove most of the DMF.



base	temp. (°C)	yield (%)[a]	remaining electrophile (%)[b]
BTPP	rt	0	74
	50	<1	18
	80	6	0
LiO*t*-Bu	rt	0	48
	50	0	4
	80	0	0
KH	rt	0	2
	50	0	2
	80	0	1
none[c]	rt	0	94
	50	4	55
	80	3	<1

[a] The yield was determined through analysis via ^{1}H NMR spectroscopy, versus an internal standard (average of two experiments). [b] The amount of unreacted electrophile was determined through GC analysis versus an internal standard (average of two experiments). [c] Ratio of nucleophile-to-electrophile: 2:1.

IX. References

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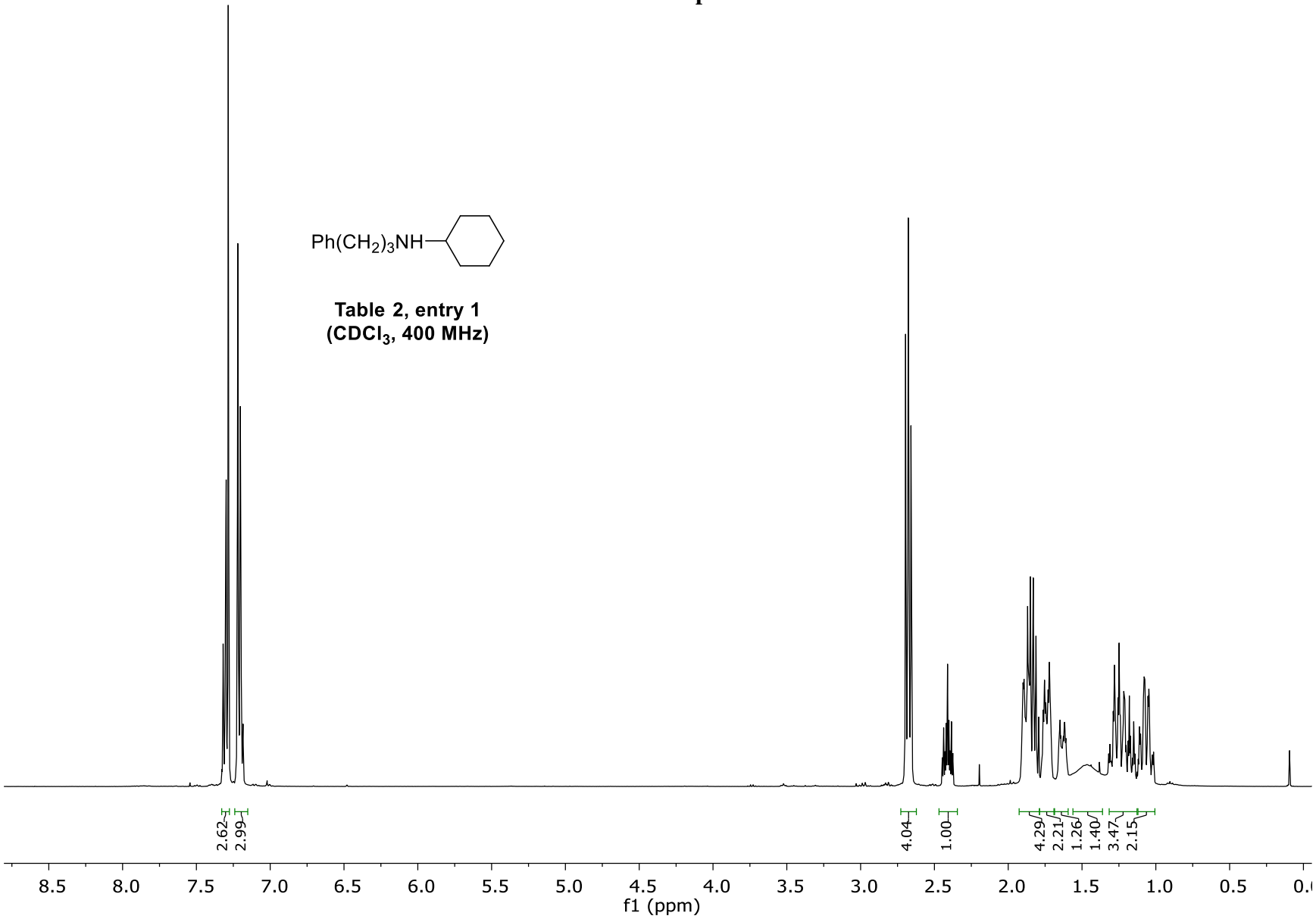
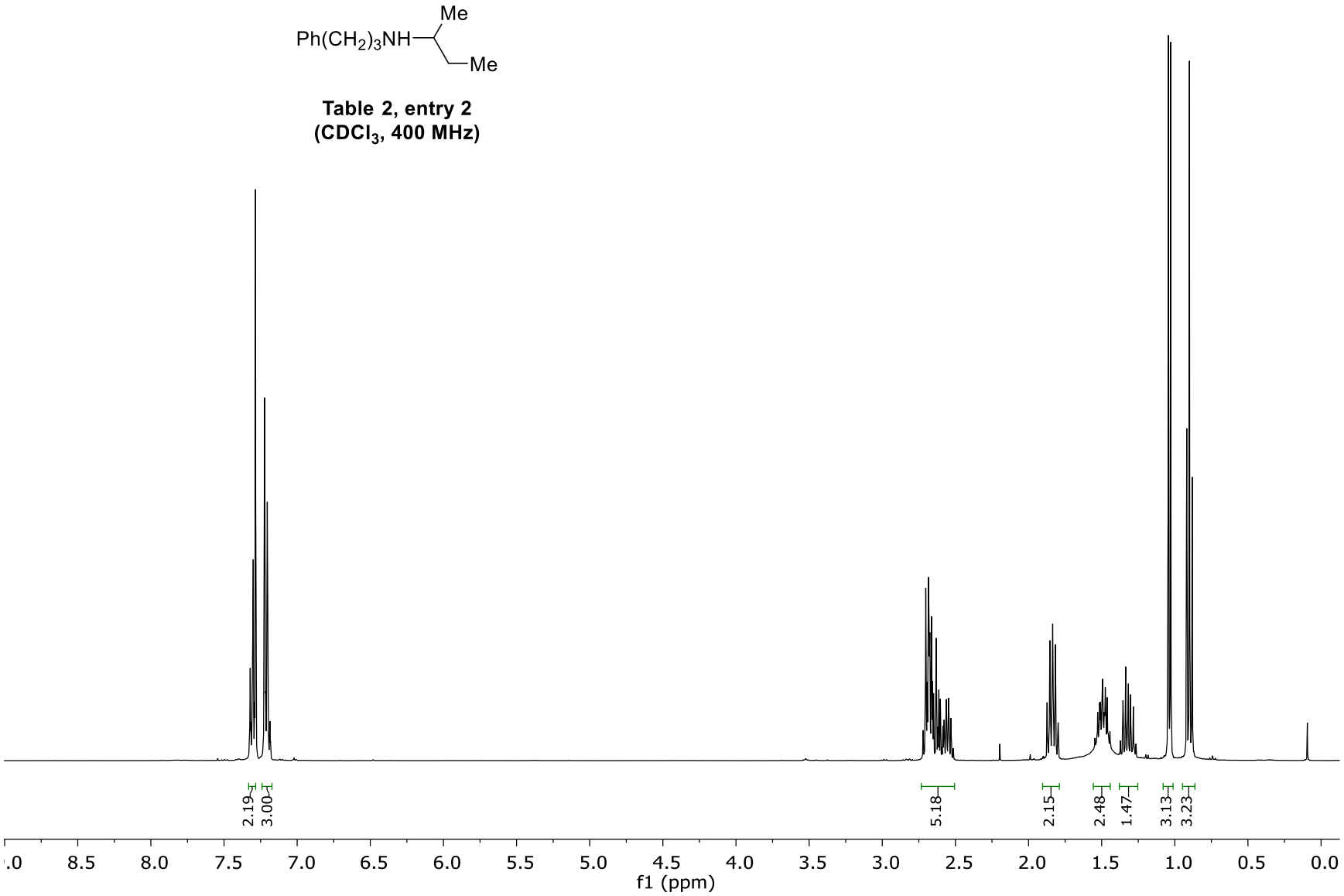
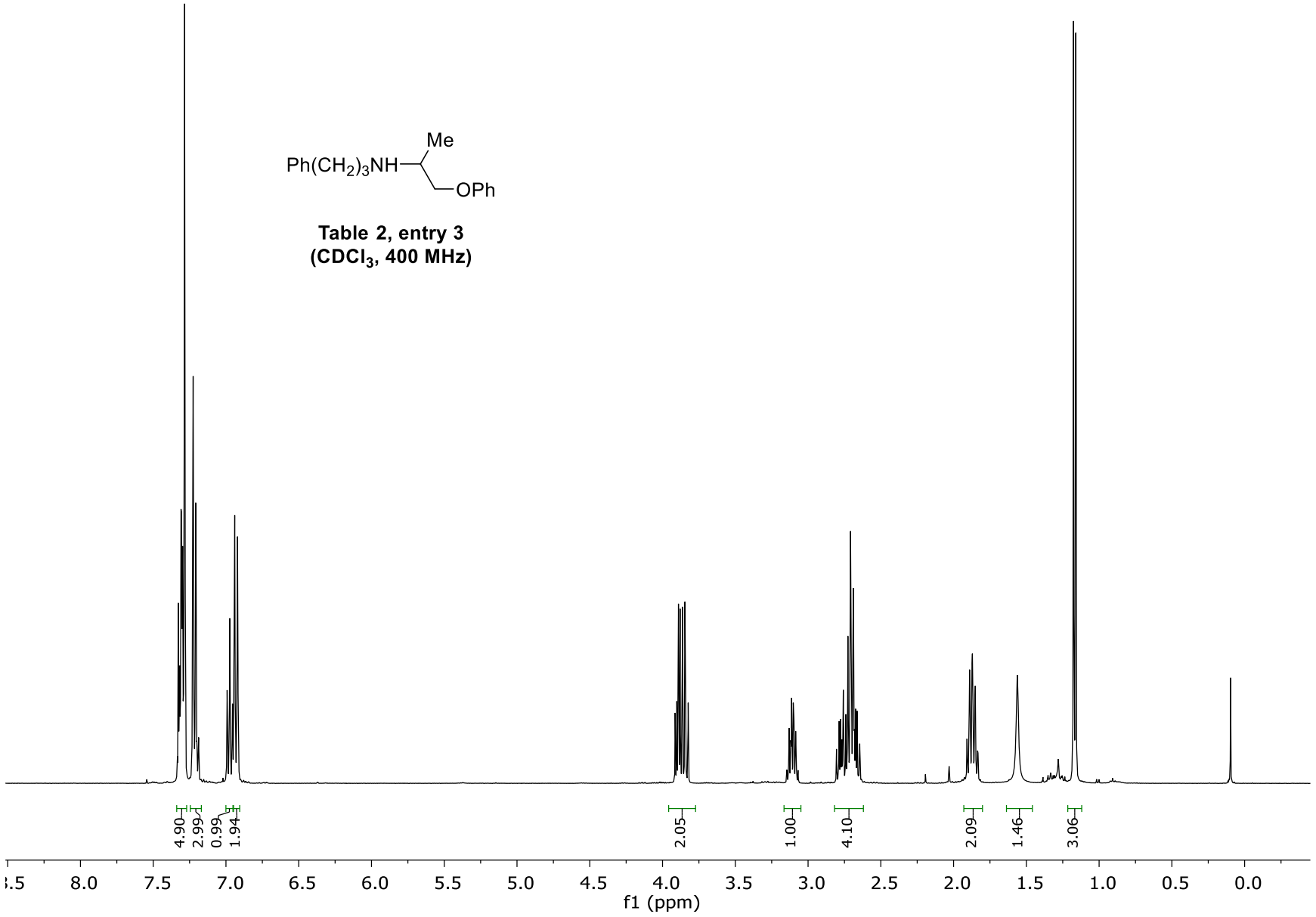
X. ^{1}H NMR Spectra




Me
Ph(CH2)3NH
Me
Table 2, entry 2
(CDCl3, 400 MHz)
2.19
3.00
5.18
2.15
2.48
1.47
3.13
3.23
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Me
Ph(CH2)3NH
OPh
Table 2, entry 3
(CDCl3, 400 MHz)
4.90
2.99
0.99
1.94
2.05
1.00
4.10
2.09
1.46
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

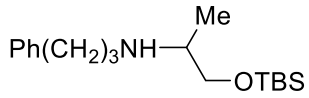


Table 2, entry 4
($CDCl_3$, 400 MHz)

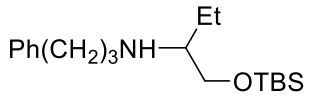


Table 2, entry 5
($CDCl_3$, 400 MHz)

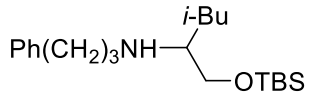


Table 2, entry 6
($CDCl_3$, 400 MHz)

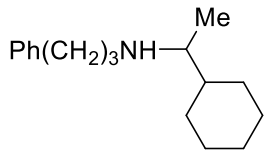


Table 2, entry 7
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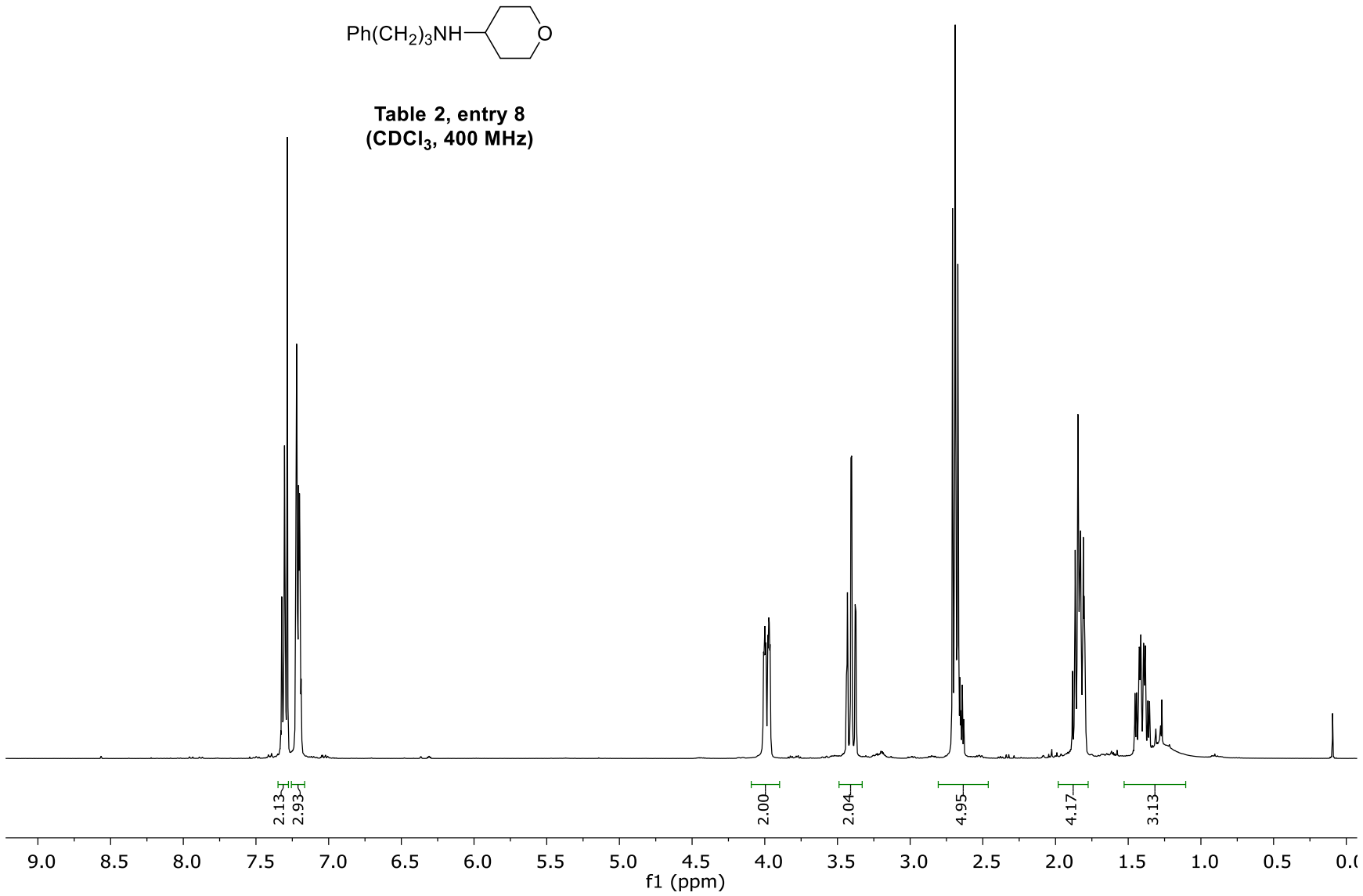
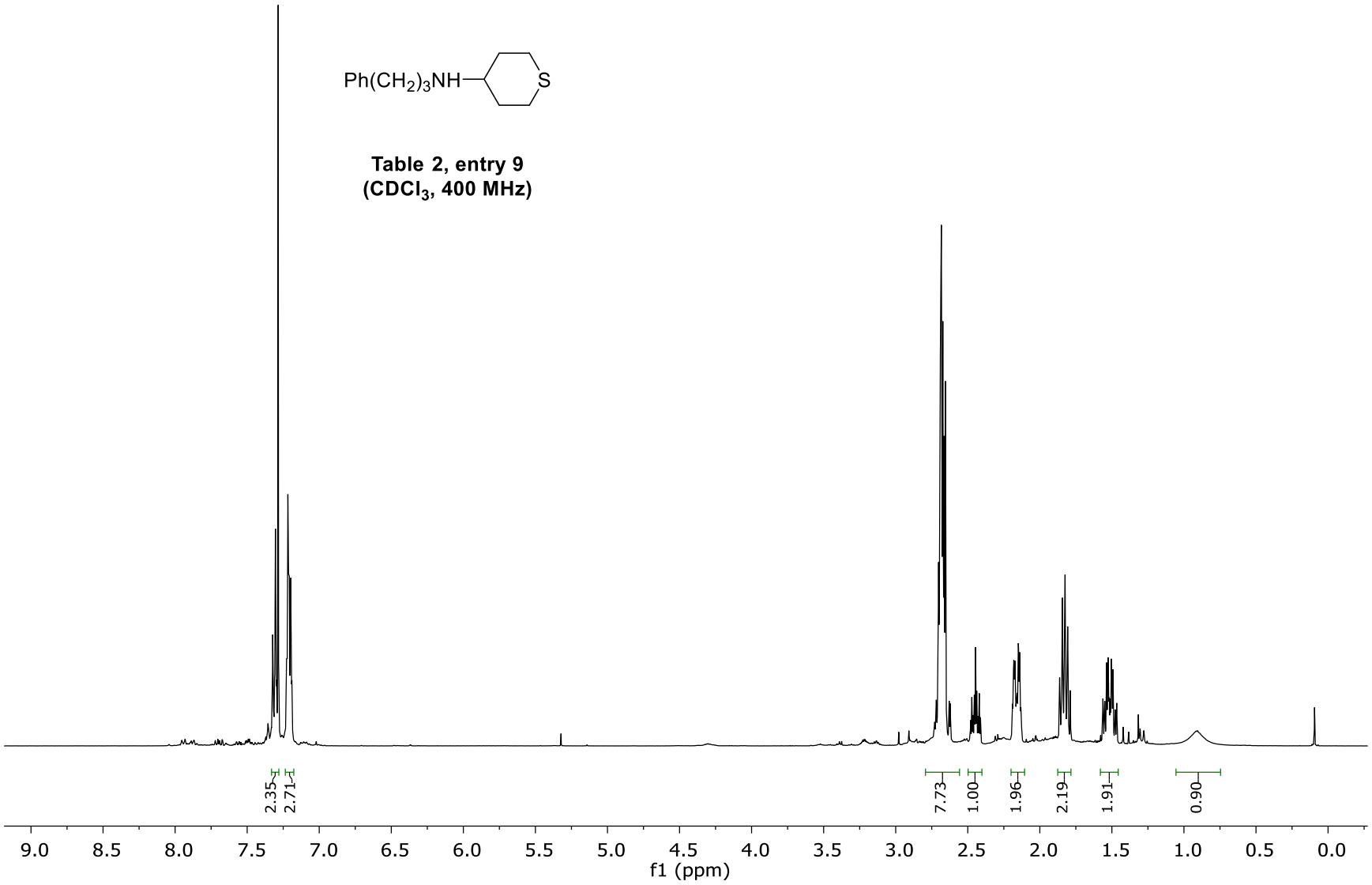
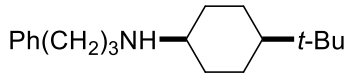

Ph(CH2)3NH
O
Table 2, entry 8
(CDCl3, 400 MHz)
2.13
2.93
2.00
2.04
4.95
4.17
3.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Ph(CH2)3NH
S
Table 2, entry 9
(CDCl3, 400 MHz)
2.35
2.71
7.73
1.00
1.96
2.19
1.91
0.90
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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($CDCl_3$, 400 MHz)

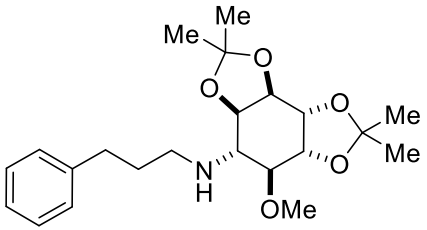
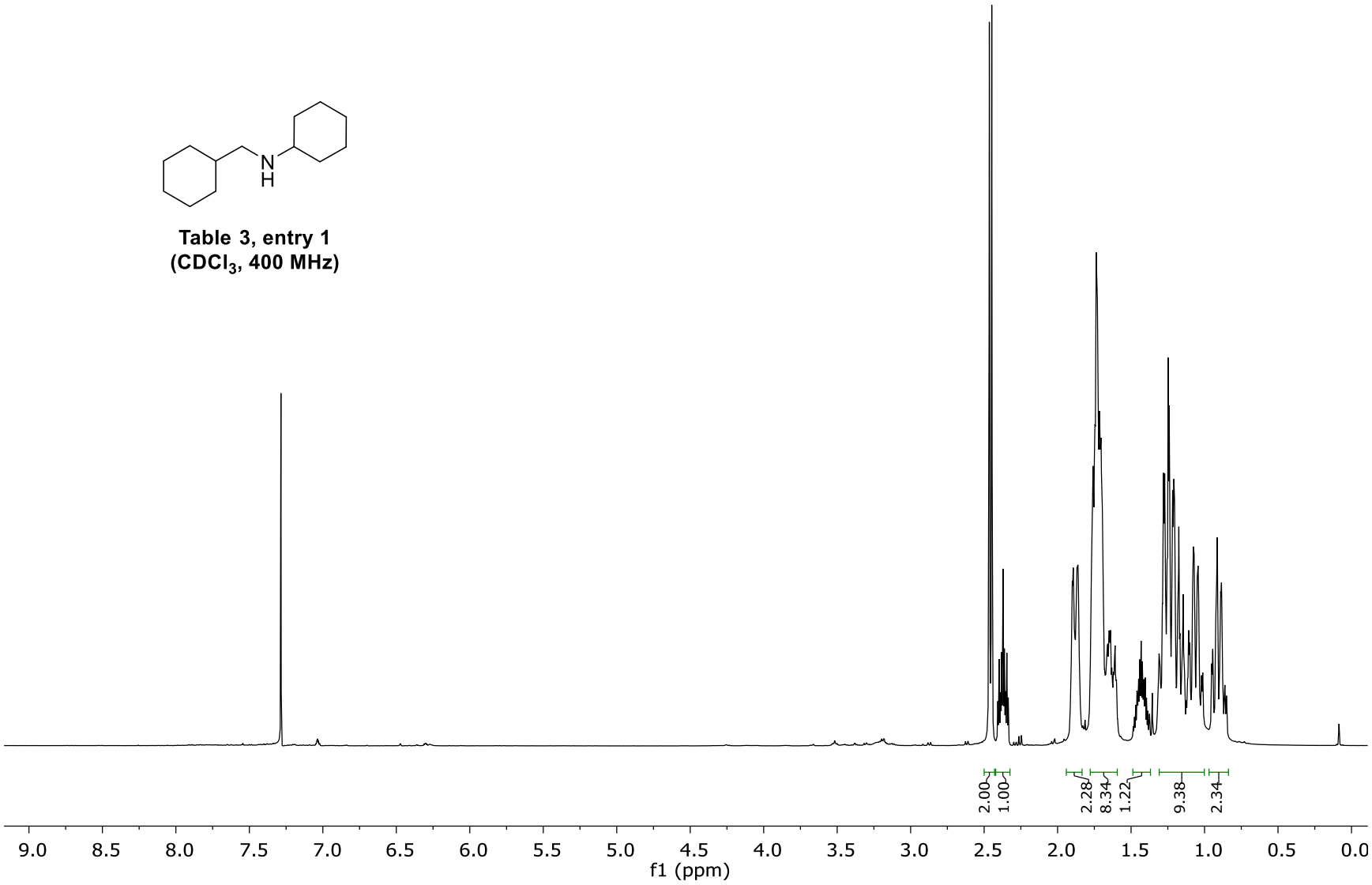
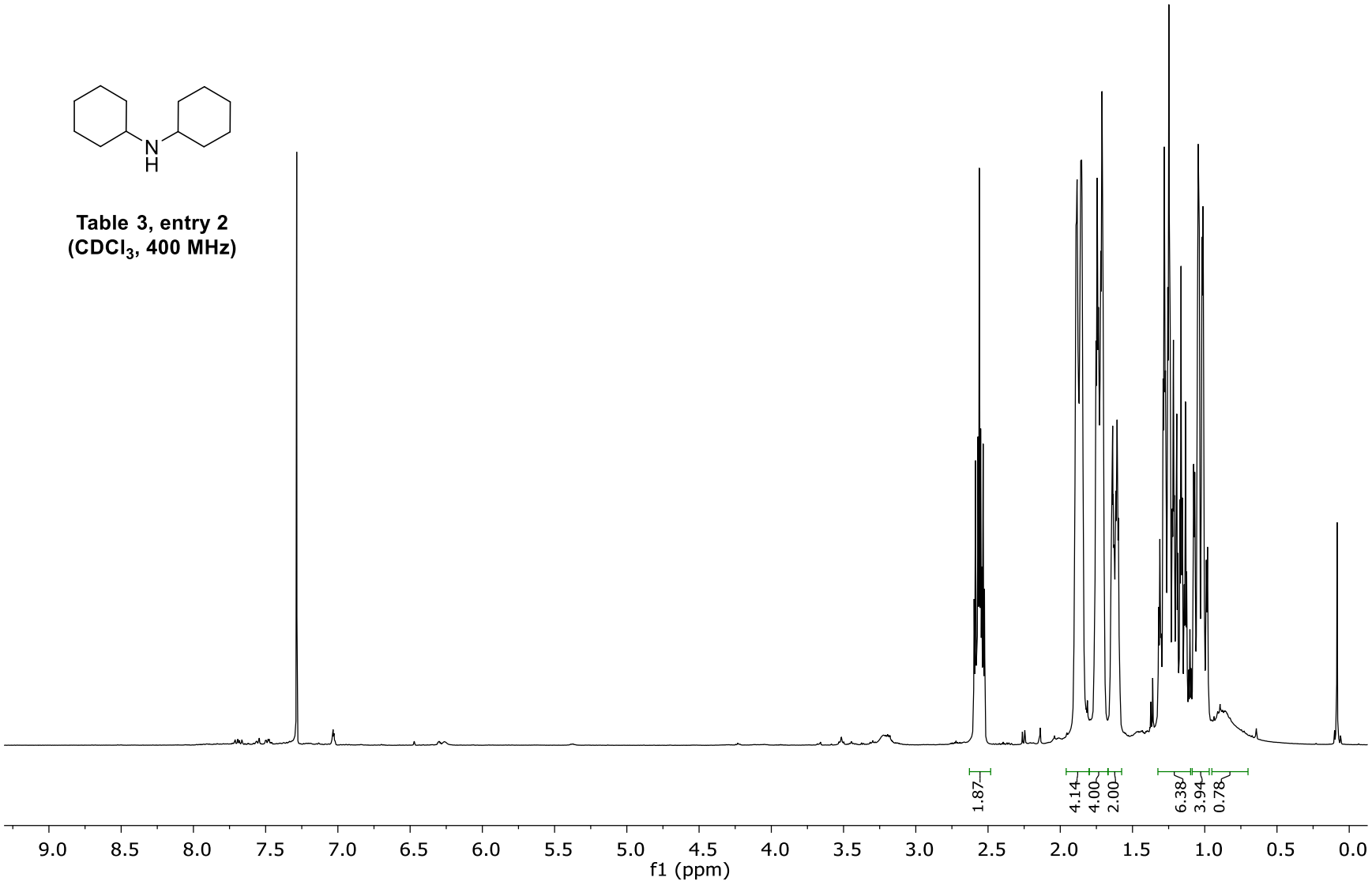
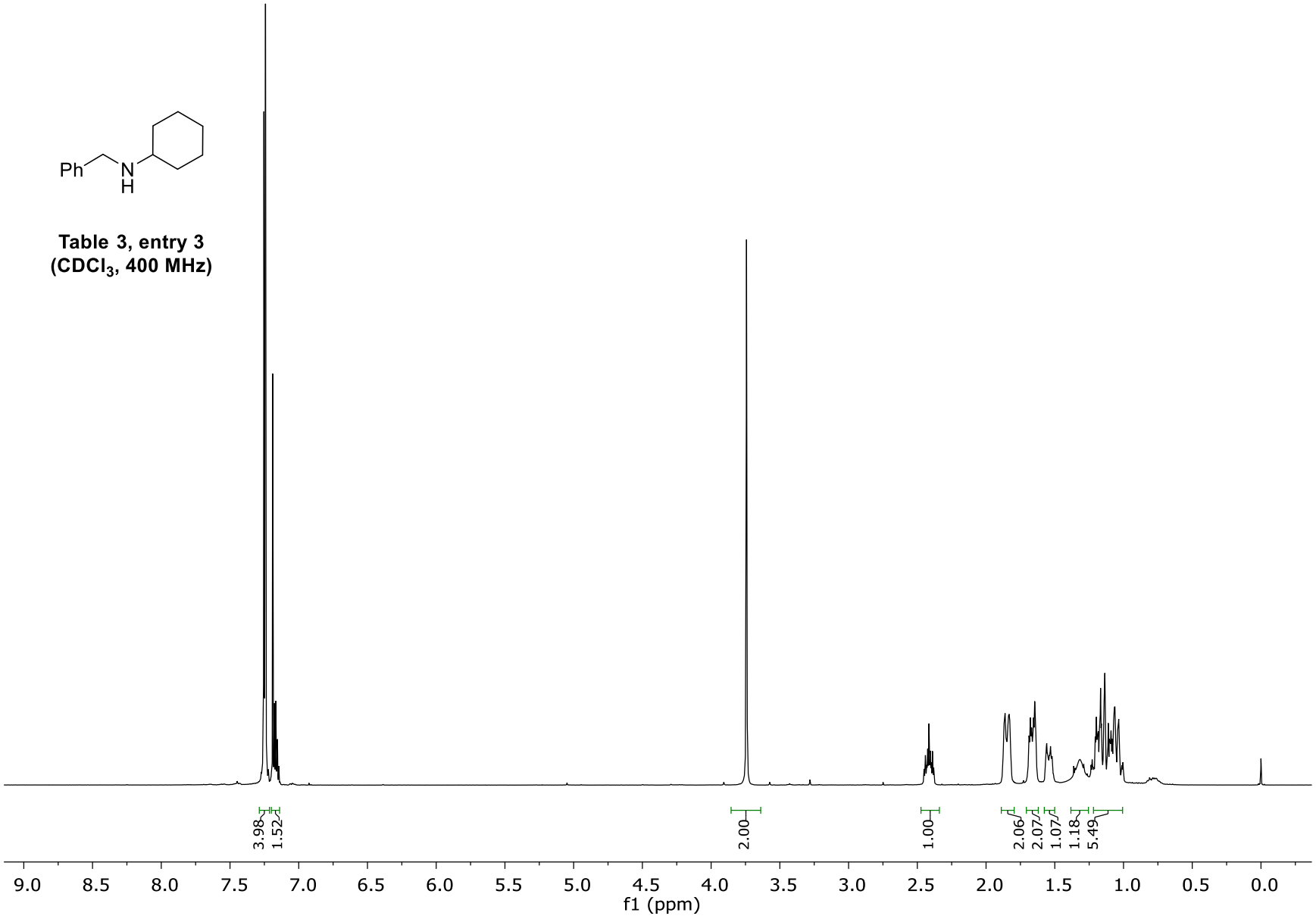
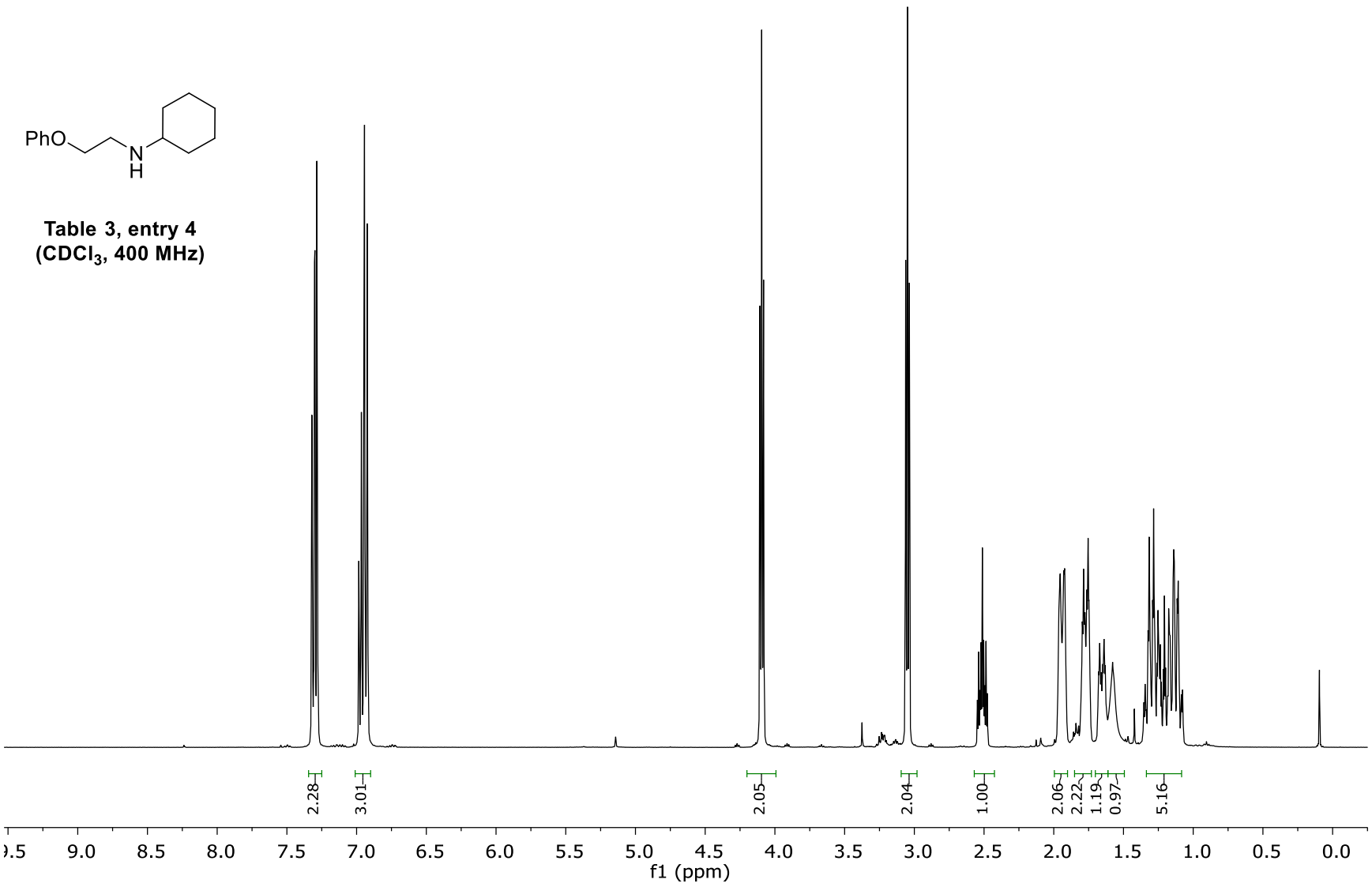


Table 2, entry 11
($CDCl_3$, 400 MHz)


N
H
Table 3, entry 1
(CDCl3, 400 MHz)
2.00
1.00
2.28
8.34
1.22
9.38
2.34
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


N
H
Table 3, entry 2
(CDCl3, 400 MHz)
1.87
4.14
4.00
2.00
6.38
3.94
0.78
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ph
N
H
Table 3, entry 3
(CDCl3, 400 MHz)
3.98
1.52
2.00
1.00
2.06
2.07
1.07
1.18
5.49
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


PhO
N
H
Table 3, entry 4
(CDCl3, 400 MHz)
2.28
3.01
2.05
2.04
1.00
2.06
2.22
1.19
0.97
5.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

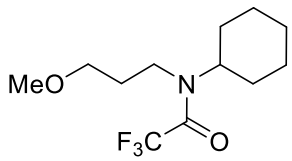


Table 3, entry 5
(d_6-DMSO, 500 MHz, 130 °C)

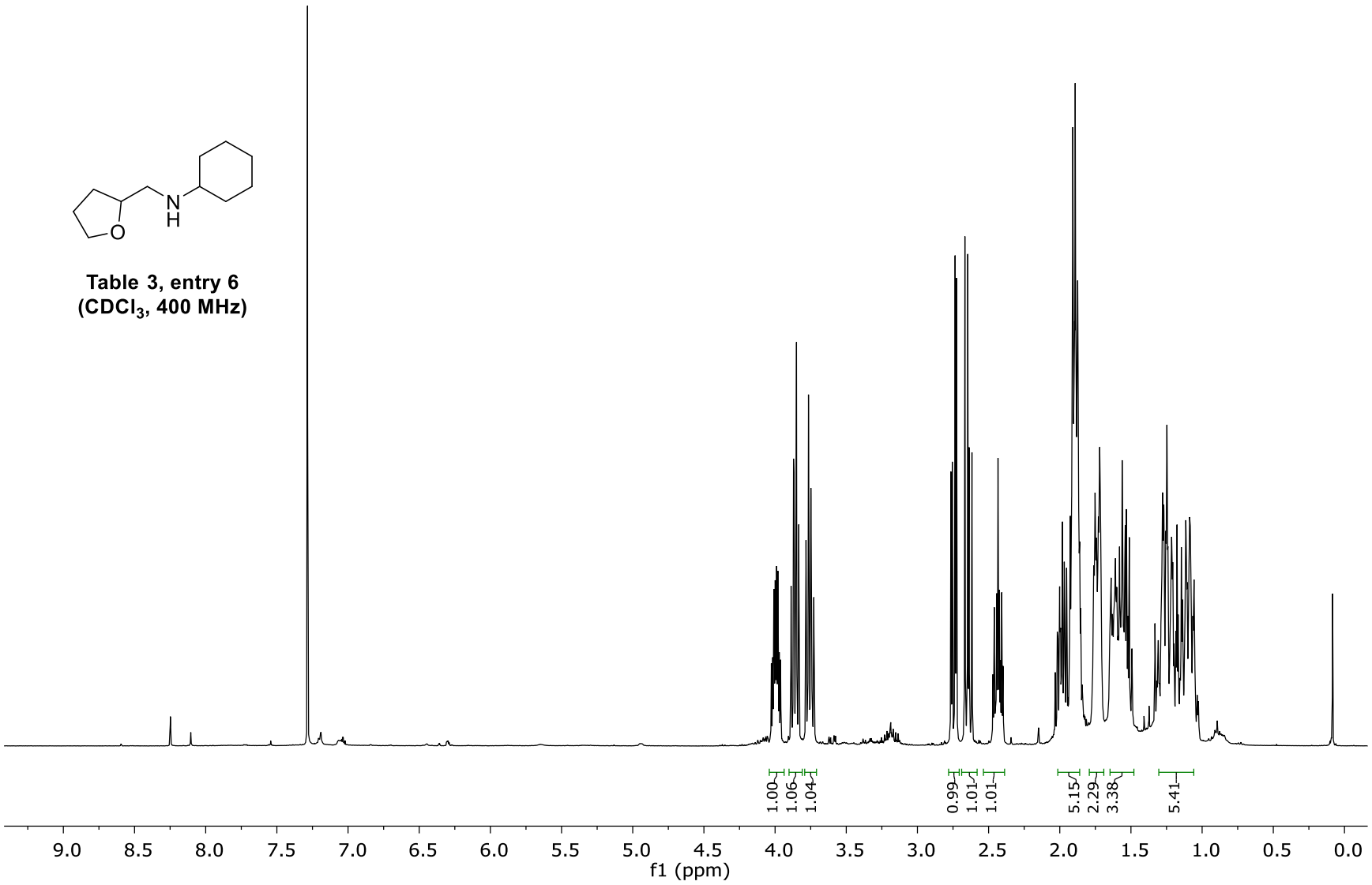


Table 3, entry 6
(CDCl3, 400 MHz)
1.00
1.06
1.04
0.99
1.01
1.01
5.15
2.29
3.38
5.41
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

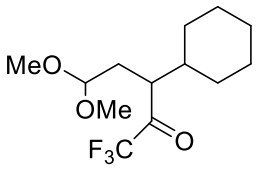


Table 3, entry 7
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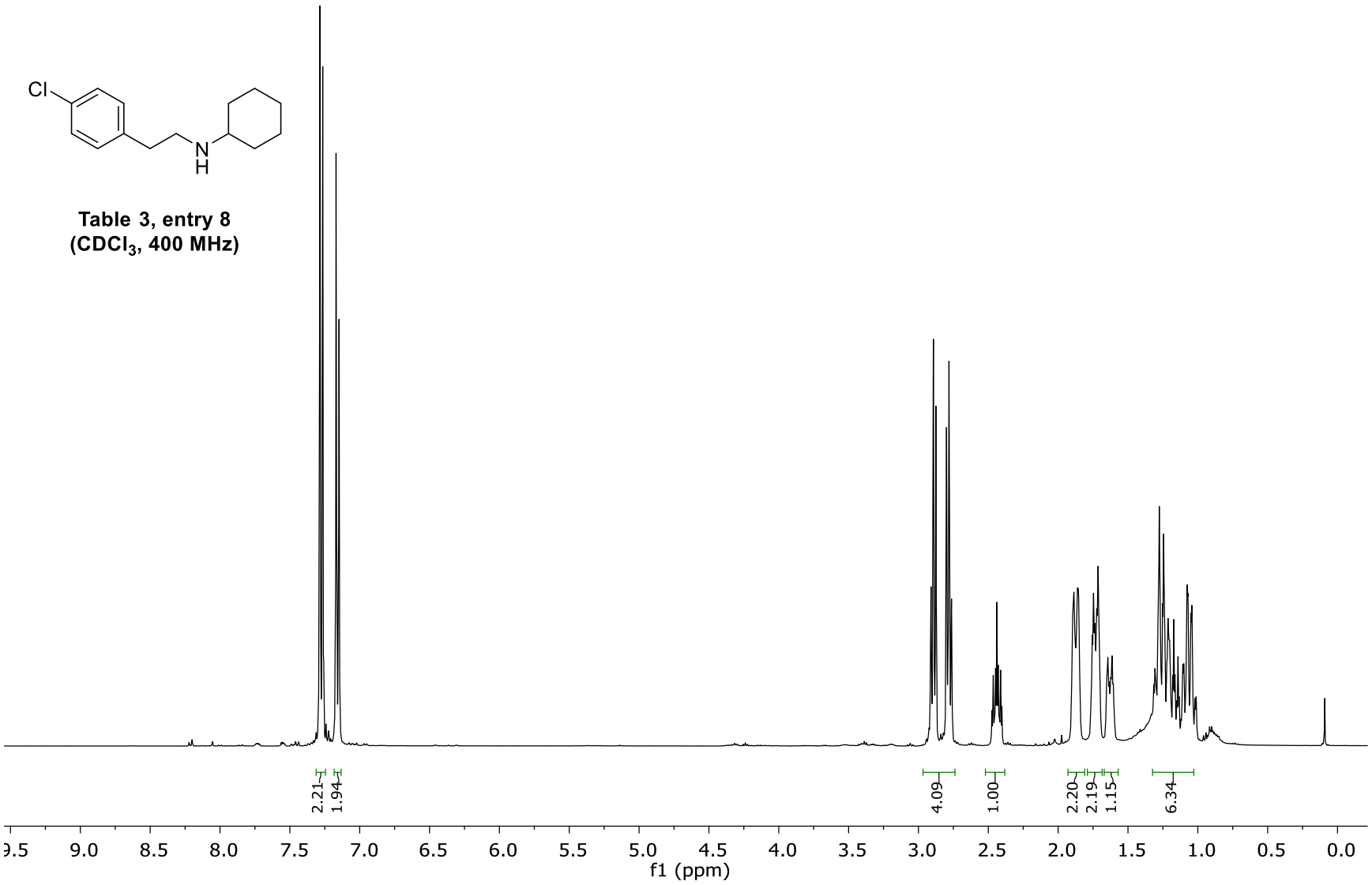
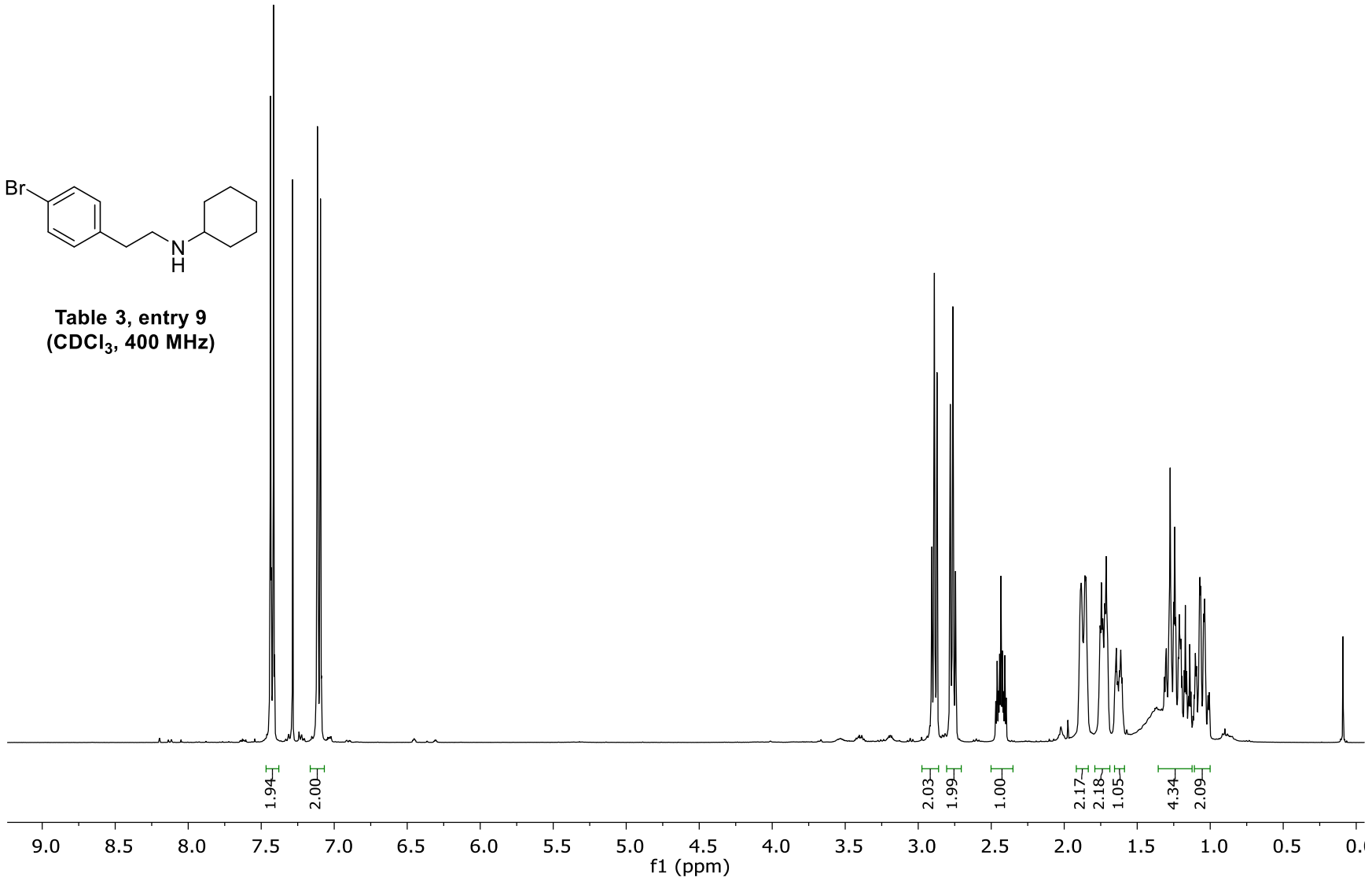

Cl
N
H
Table 3, entry 8
(CDCl3, 400 MHz)
2.21
1.94
4.09
1.00
2.20
2.19
1.15
6.34
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Br
N
H
Table 3, entry 9
(CDCl3, 400 MHz)
1.94
2.00
2.03
1.99
1.00
2.17
2.18
1.05
4.34
2.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

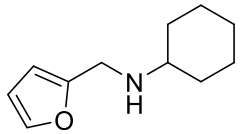


Table 3, entry 10
($CDCl_3$, 400 MHz)

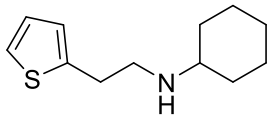
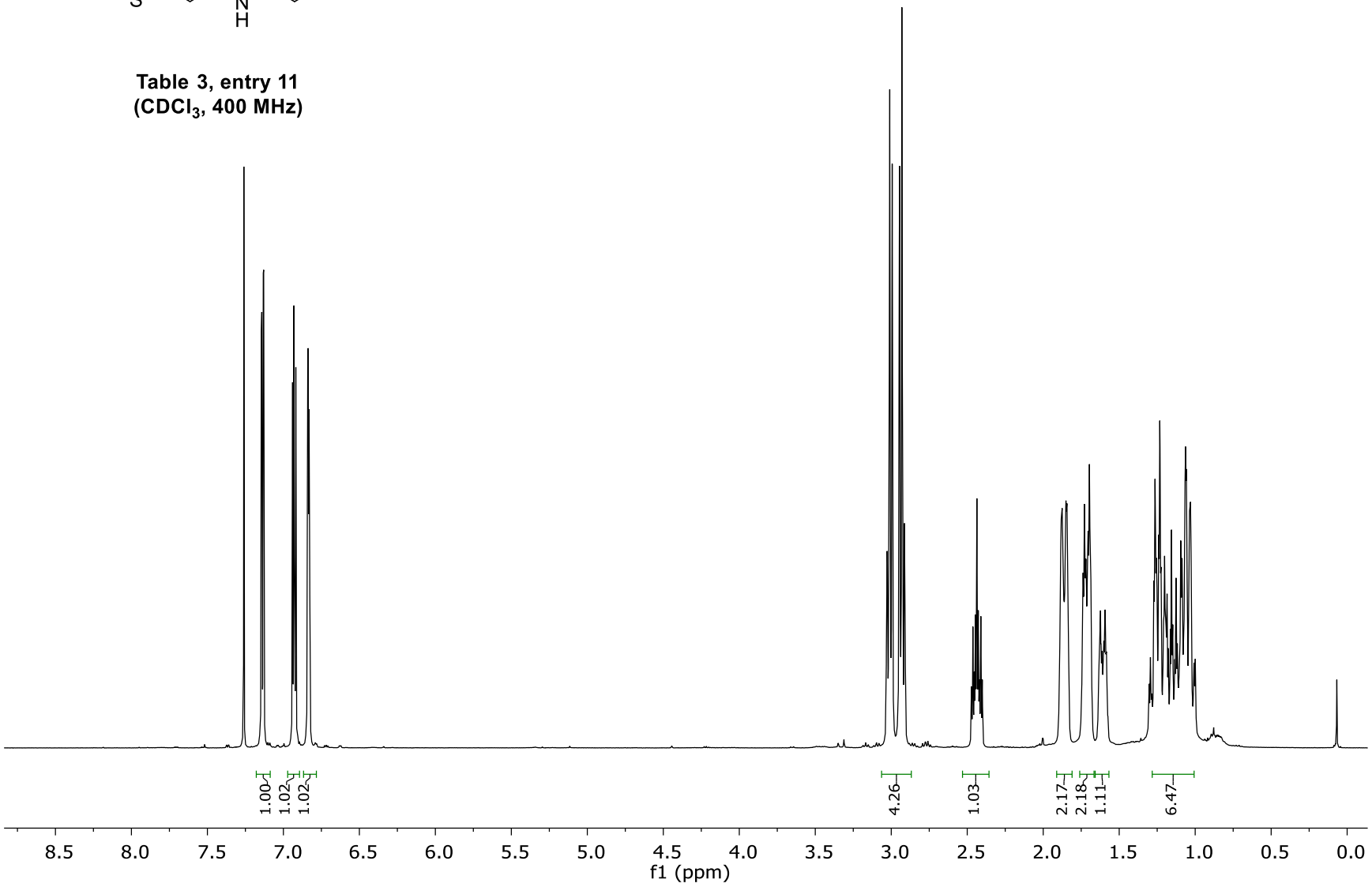
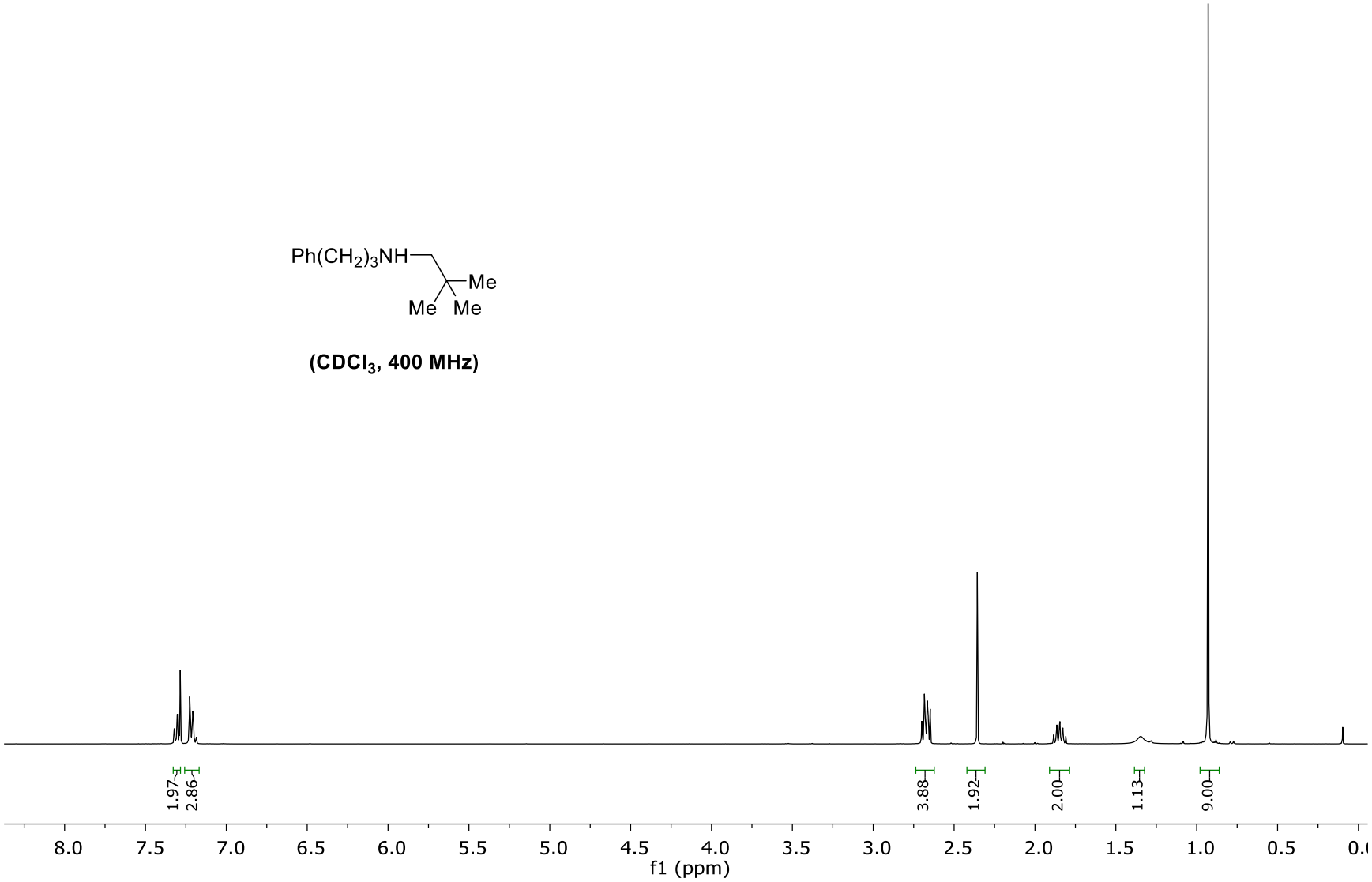
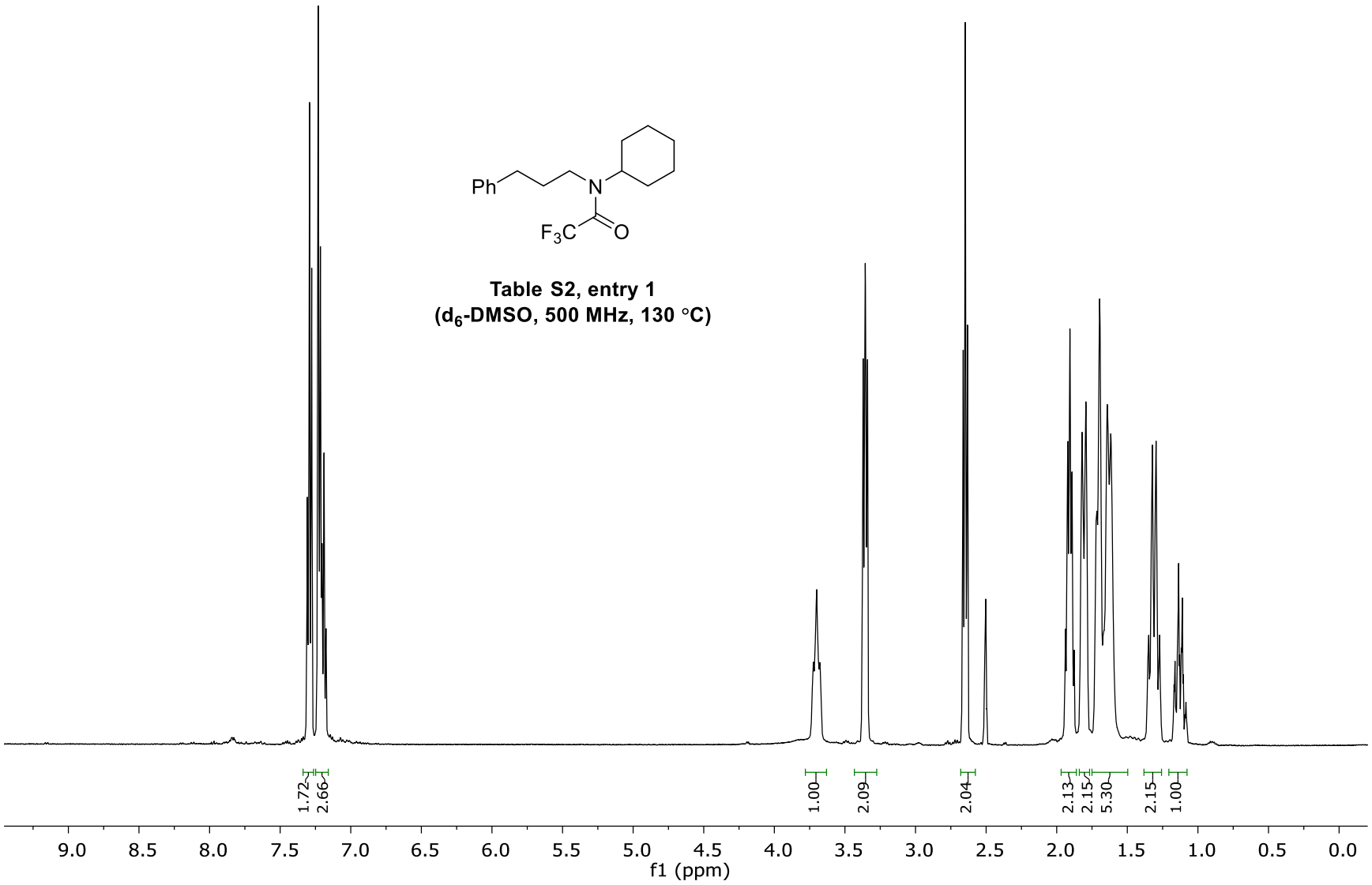


Table 3, entry 11
($CDCl_3$, 400 MHz)




Ph(CH2)3NH
Me
Me
Me
(CDCl3, 400 MHz)
1.97
2.86
3.88
1.92
2.00
1.13
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Ph
N
F3C
O
Table S2, entry 1
(d6-DMSO, 500 MHz, 130 °C)
1.72
2.66
1.00
2.09
2.04
2.13
2.15
5.30
2.15
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

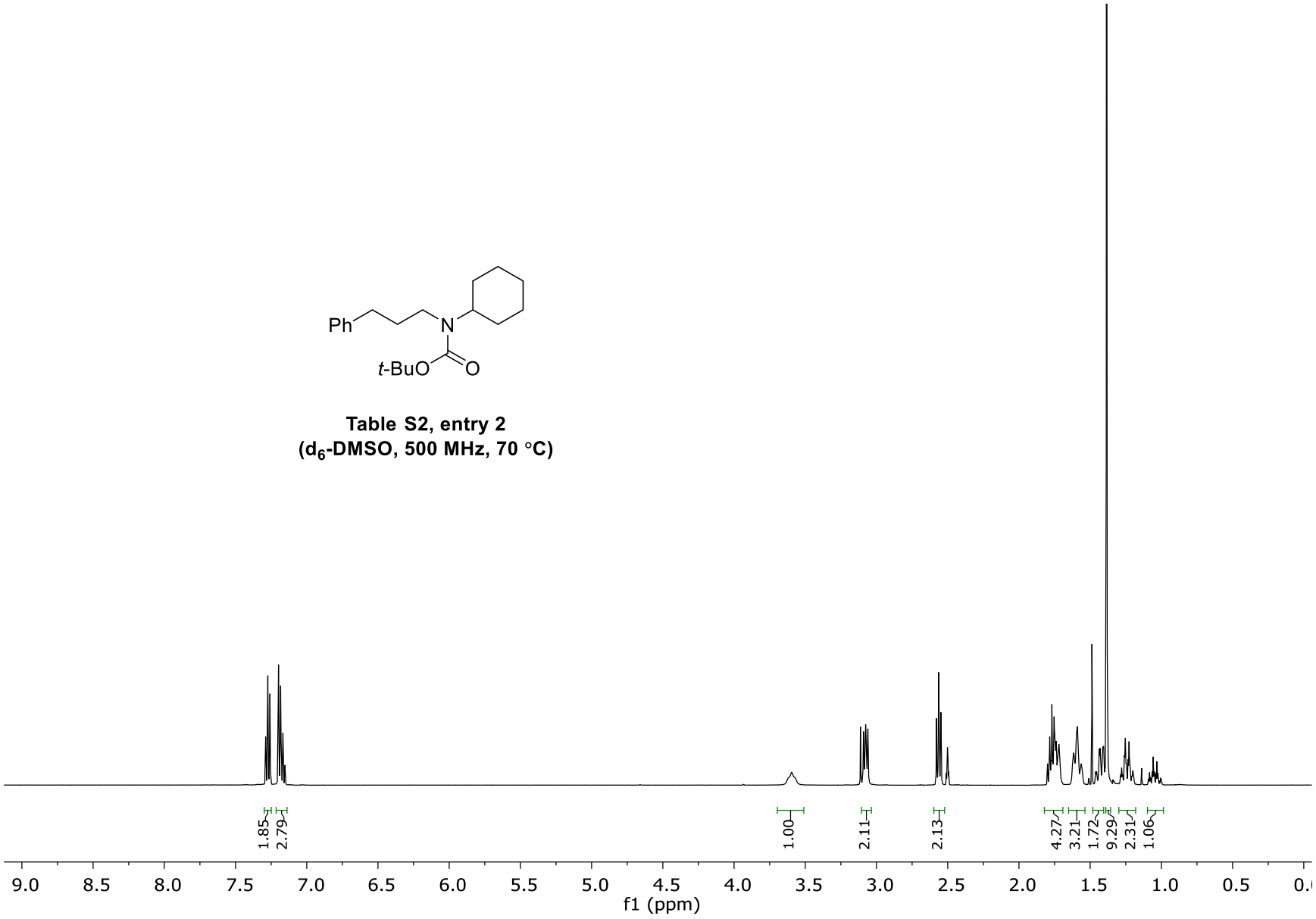


Table S2, entry 2
(d_6-DMSO, 500 MHz, 70 °C)

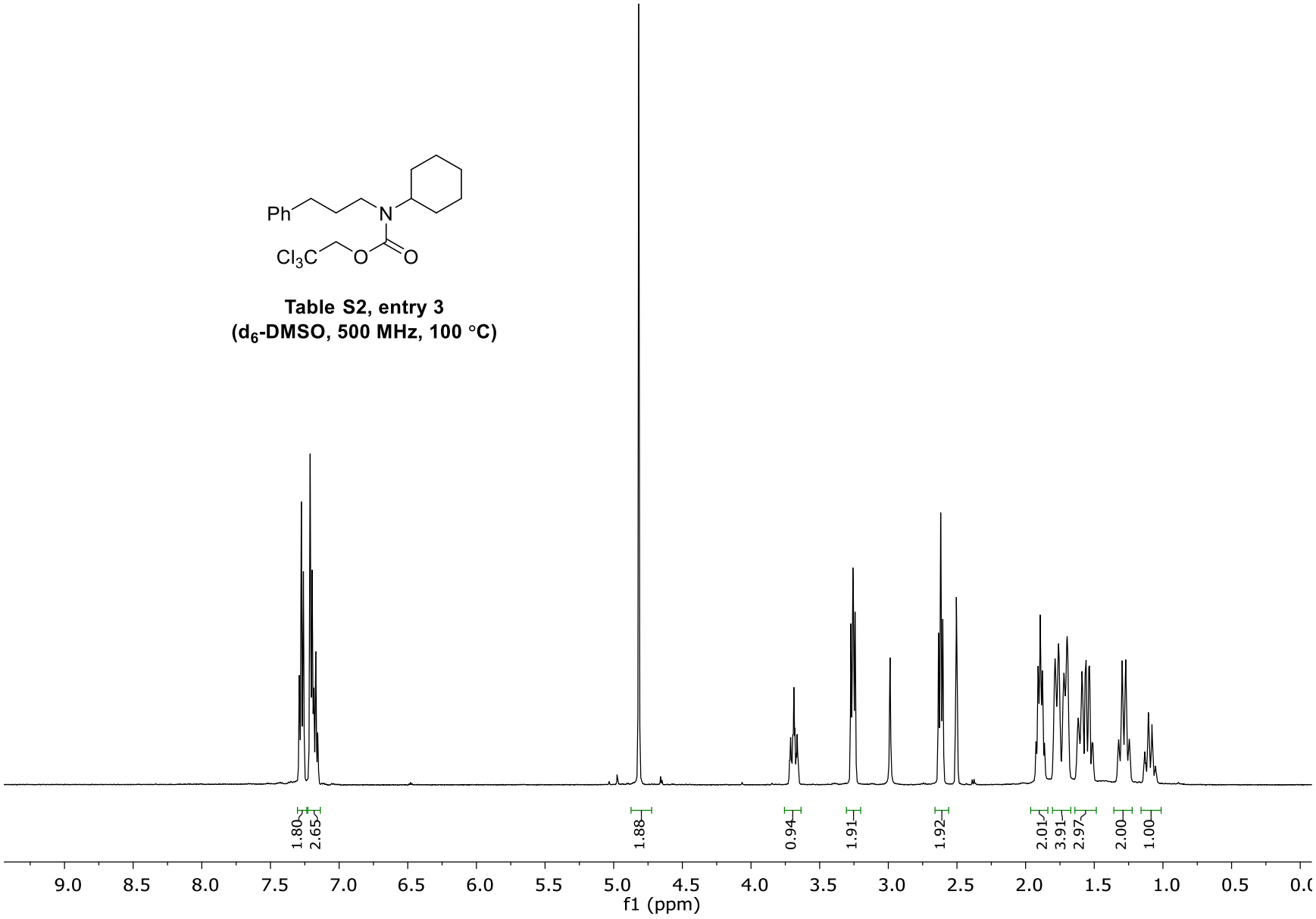
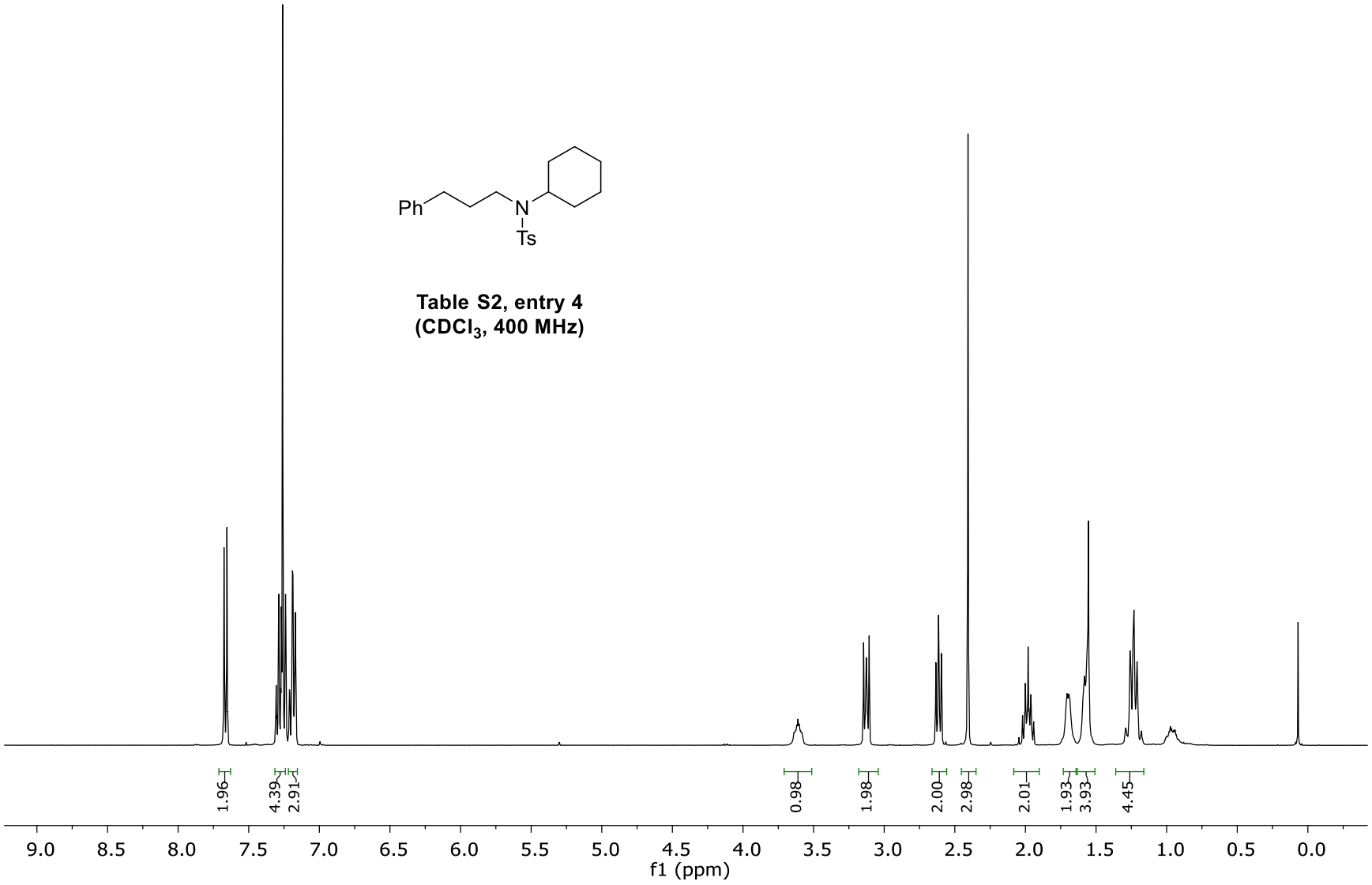


Table S2, entry 3
(d_6-DMSO, 500 MHz, 100 °C)


Ph
N
Ts
Table S2, entry 4
(CDCl3, 400 MHz)
1.96
4.39
2.91
0.98
1.98
2.00
2.98
2.01
1.93
3.93
4.45
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

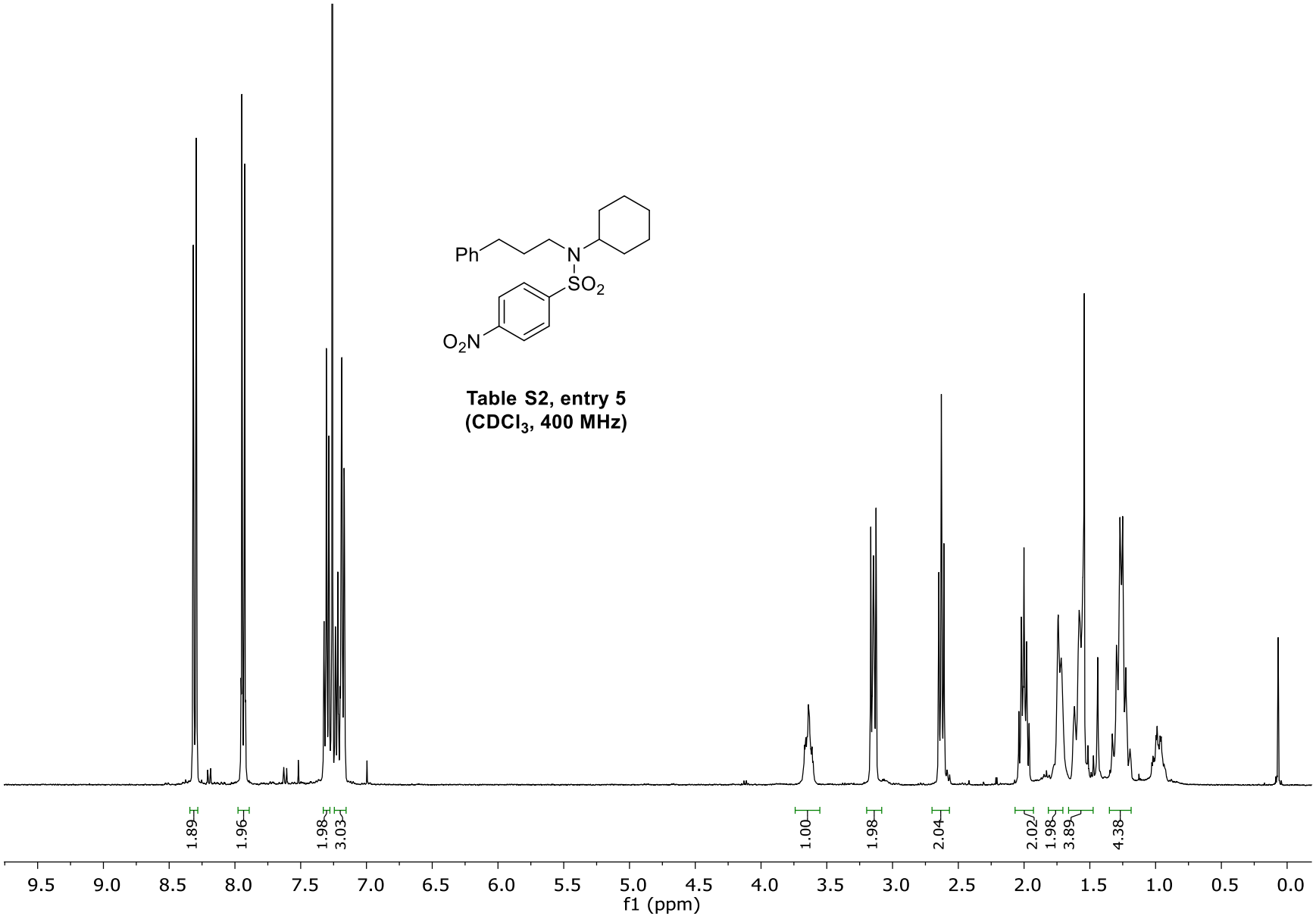


Table S2, entry 5
($CDCl_3$, 400 MHz)